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Exergy and process analysis to assess primary energy resource consumption: a critical review

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“Energy is the currency around which we should be basing
our economic forecasts, not money supply.”
Mark O. Hatfield, United States Senator

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Abstract

A sustainable development is not an easy task to pursue, and, furthermore, it seems always more requested that anything comes with a tag. The case of primary energy resource consumption needs careful consideration since it is of vital importance for the global society, and assessing exactly the depletion of these resources can be a really hard job.

It has to be noted that natural resource scarcity cannot be estimated using thermodynamics tools, consequently, depletion, which is linked to scarcity, is not measurable and only the resource consumption assessment can be pursued.

Among the aims of this work, the comparative analysis of the thermodynamic numeraires, in order to understand which one is the more appropriate for resource consumption assessment. Finally, even if entropy appeared a good alternative, exergy results being the best fit when resource consumption must be assessed, since it can easily include quantity and quality of any kind of resource.

Another objective of this work was to analyse the kind of process analyses that are employed to assess natural resource use. More methods than the quantity of thermodynamic numeraires have been found, but no one could be explicitly chosen as the best one.

keywords: exergy, process analysis, resources consumption

Italian Abstract

Perseguire uno sviluppo sostenibile non è facile, inoltre, sembra che sia sempre più richiesta un'etichetta appropriata su ogni cosa. Le risorse energetiche primarie sono di un'importanza vitale per la società globale e stimarne in maniera esatta il loro esaurimento non è un lavoro semplice.
Bisogna inoltre notare che non è possibile stimare la scarsità con gli strumenti della termodinamica, per cui, poiché l'esaurimento delle risorse dipende dalla loro scarsità, è possibile calcolarne solo il consumo.
In questo lavoro si è cercato di dimostrare perché bisogna usare l'exergia come indicatore per la stima del consumo di risorse energetiche primarie, mettendola a confronto con le altre numerarie termodinamiche (massa, energia ed entropia). Nonostante l'entropia appaia come una valida scelta, dall'analisi comparativa si evince che l'exergia è l'indicatore che meglio misura le risorse naturali e il loro consumo, perché può tener conto della quantità e della qualità di una risorsa in maniera più intuitiva.
Un altro obiettivo di questo lavoro è stato analizzare i diversi tipi di analisi di processo impiegati per valutare il consumo di risorse naturali. In letteratura sono stati trovati un numero di metodi maggiore delle numerarie analizzate, ma non si è riusciti a trovare quale tra questi possa rappresentare la scelta migliore.

parole chiave: exergia, analisi di processo, consumo di risorse

Extract in Italian

Con questo lavoro termina un percorso di studi volto all'analisi dei sistemi energetici, con l'attenzione al fatto che la parola 'energia' è sempre più presente all'interno del linguaggio comune, ma assegnarle un valore appropriato appare molto difficile. Questo lavoro di tesi è stato condotto con l'obiettivo di fare luce sui metodi e sulle numerarie utilizzate per stimare il consumo di risorse energetiche primarie, cercando di racchiudere in un unico testo alcuni tra i metodi più diffusi nell'ambito del consumo delle risorse energetiche.

Nel primo capitolo si è definito, inizialmente, cosa vuol dire ecosistema, cosa si intende per risorse naturali e come queste si distinguano: flussi e depositi/riserve. Successivamente si è discusso della differenza tra le parole 'uso', 'consumo' ed 'esaurimento', tipicamente accoppiate alla parola risorse. Mettendo in luce che ciò che si può facilmente misurare è il consumo di una risorsa naturale, mentre dare un valore numerico al suo esaurimento prevede che si abbiano informazioni ulteriori riguardanti la fonte da cui proviene. Poi, sono state passate in rassegna le numerarie termodinamiche impiegate per misurare le risorse naturali e stimarne il consumo. Si è analizzato come sono definite, come si calcolano e che applicazioni possono avere, la massa, l'energia, l'entropia e l'exergia. Questa parte viene conclusa con una comparazione di dette numerarie, dove entropia ed exergia hanno all'incirca le stesse potenzialità come unità di misura nella stima del loro consumo. Ma, poiché il calcolo dell'exergia include sia il bilancio di massa, sia il bilancio energetico, sia la generazione entropica e inoltre, risulta essere più intuitiva dell'entropia, l'exergia viene indicata come miglior termine per la stima del consumo di risorse.

Nel secondo capitolo è trattata l'analisi di processo applicata al consumo di risorse naturali. È fatta una descrizione di come quest’approccio va impiegato e in quali casi è applicabile, il tutto accompagnato da una lista di vantaggi e svantaggi legati a tale metodologia. Tra gli ultimi sono elencati gli errori dovuti al troncamento del sistema analizzato, poiché gli input risalendo a monte della filiera produttiva diventano numerosi ma, talvolta, senza rilevanza numerica, per cui si ha la tendenza ad escluderli, se di entità molto ridotta. A livello informativo, sono state esposte le possibili scelte sull'analisi di processo, quali analisi input-output e analisi ibride. Si sono, quindi, analizzate le analisi di processo che usano le numerarie descritte nel primo capitolo come unità di misura per la stima del loro consumo. La material flow analysis (MFA) per misurare il consumo di risorse si basa sul bilancio di massa di una o più sostanze, scelte tra i materiali coinvolti in un sistema, per il quale è stato scelto un volume di controllo opportuno. Le analisi energetiche vengono indicate come 'Net Energy Analysis' ('analsi energetica netta') o 'Embodied Energy ('energia grigia') Analysis'. Quest’approccio analizza la filiera degli input energetici necessari a produrre un determinato output, differenziando gli apporti energetici in 'diretti' e 'indiretti'. L'energia grigia consiste nella somma di tutti i consumi diretti e indiretti, mentre l'energia netta si ottiene dalla differenza tra il contenuto energetico e l'energia grigia (o anche 'consumo energetico cumulato') del prodotto in questione. L'analisi che ha l'entropia come numeraria ha come obiettivo minimizzare la generazione entropica ('entropy generation minimization' o EGM). La EGM segue un approccio simile alle analisi energetiche poiché considera tutte le irreversibilità che appaiono in un sistema (o in un processo) e, tramite una funzione obiettivo, tenta di minimizzarle, massimizzando l'efficienza termica del sistema (o del processo). Le analisi exergetiche, anch'esse basate sulla seconda legge della termodinamica, includono sia flussi materiali, sia flussi di energia, e hanno come obiettivo quello di minimizzare la distruzione di exergia. Quest'analisi è spesso usata nel campo dell'ecologia come in quello industriale e, ultimamente, è stata impiegata per esaminare interi settori dell'economia di più paesi. Infine si sono messi in risalto pro e contro di questi approcci ma senza dare nuovi commenti.

Nel terzo capitolo è descritta la teoria termoeconomica, la quale ha come scopo il riunire la termodinamica con l'economia. Giacché molti dei problemi industriali sono analizzabili con approcci sia termodinamici sia economici, all'interno di questa teoria si definisce il costo exergetico in modo da poter passare con facilità dal concetto di ottimizzazione termodinamica a quello di ottimizzazione economica dei costi. Il costo exergetico è definito come la differenza tra il contenuto exergetico degli input necessari per produrre un certo output, dopo aver precisato il sistema di produzione, il volume di controllo e il livello di disaggregazione.

Il quarto capitolo contiene l'analisi dei metodi, apparentemente più diffusi, che fanno uso dell'exergia per stimare il consumo di risorse naturali. Per ogni metodo si ha una breve definizione, seguita dalle 'categorie d'impatto' incluse dalla metodologia, corredate da un elenco dei possibili campi applicativi. Primo paradigma descritto è il **C**umulative **Ex**ergy **C**onsumption, CExC ('consumo cumulato di exergia'), il quale tiene conto dell'exergia contenuta in tutti gli input di un processo. Le categorie d'impatto considerate sono tutte le risorse naturali, rinnovabili e non rinnovabili. Secondo paradigma descritto è il **T**hermo **E**cological **C**ost ('costo termo ecologico') TEC, il quale considera solo gli input di risorse non rinnovabili, categorizzandole ulteriormente in 'combustibili' ('fuel resources') e in minerali ('mineral resources'). Questo paradigma si basa sul fatto che, solo quello che non è rinnovabile è esauribile, per tale motivo bisogna stimarne il consumo; la differenza tra risorse energetiche e risorse minerali deriva dal fatto che i minerali non posso essere rimpiazzabili mentre le l'energia può essere ottenuta tramite fonti rinnovabili. Terzo paradigma è l'**E**xergetic **L**ife **C**ycle **A**ssessment, ELCA ('valutazione exergetica del ciclo di vita'), il quale vede accoppiata la metodologia dell'analisi del ciclo di vita all'exergia. Basicamente l'ELCA è uguale al CExC con l'aggiunta di considerare esplicitamente le fasi della vita di un sistema generico: produzione o costruzione, utilizzo, smantellamento o dismissione. Il quarto paradigma descritto è il CEENE, **C**umulative **E**xergy **E**xtraction from the **N**atural **E**nvironment ('exergia cumulata estratta dall'ambiente'), il quale considera oltre alle categorie d'impatto del CExC, anche l'occupazione del suolo. Questa categoria incorpora l'impossibilità dell'ambiente di utilizzare il flusso exergetico proveniente dal Sole per alimentare la fotosintesi e far crescere le piante. Infatti, la mancata produzione di biomassa e l'occupazione di terreno sono considerate la stessa cosa e sono incluse all'interno della categoria 'land resources' ('risorse del suolo'). Una leggera differenza del CEENE, rispetto a tutti gli altri metodi, si ha nell'ambiente di riferimento, solo per quanto riguarda la composizione del composto chimico di riferimento per l'alluminio. Quinto e ultimo paradigma descritto è l'**E**xtended **E**xergy **A**ccounting, EEA ('analisi exergetica estesa'), il quale può essere visto come un'estensione del paradigma CExC, poiché, oltre a materiali ed energia, include anche contributi di manodopera, capitali e costi di rimedio ai danni ambientali. Per tener conto di tutti questi fattori sono utilizzati degli 'equivalenti exergetici' che permettono di convertire tutti questi termini in exergia e di avere la possibilità di sommarli tra loro impiegando la stessa unità di misura. Per tutti i paradigmi, sono state messe a confronto le caratteristiche principali e da quest’analisi si evince che tra i vari metodi non c'è una completa coerenza, né nella scelta delle categorie d'impatto o delle risorse naturali da considerare, né nella scelta dei confini. In aggiunta si sono evidenziati alcuni dei vantaggi e svantaggi di ogni metodo. Infine, è proposto un metodo alternativo rispetto a quelli analizzati in precedenza, nel quale si mantiene la visione della metodologia TEC, ma includendo la manodopera tra le categorie d'impatto, prendendo spunto dal paradigma EEA. In questa metodologia, in effetti, si propone un metodo per calcolare il costo exergetico medio della manodopera, dopo aver ipotizzato che una società abbia come prodotto ultimo le sole ore di vita.

Nel quinto capitolo si è considerato l'utilizzo di un semplice cavo elettrico di rame per calcolarne, impiegando i diversi paradigmi analizzati nel quarto capitolo, le risorse consumate. Inoltre si è cercato di trovare il valore ottimale del diametro del cavo in modo tale da minimizzare il consumo di risorse.

Per questo esempio si è creato un modello molto semplificato del cavo elettrico e delle due filiere che producono, una il cavo e l'altra l'energia elettrica. Inoltre, si è adottato l'approccio dell'analisi del ciclo di vita, considerando per tutti i metodi sia la fase di costruzione sia la fase di utilizzo, ad eccezione dell'EEA che considera anche la fase di dismissione. Le curve ottenute per ogni paradigma, variando il valore del diametro del cavo elettrico, hanno forme simili alle curve di costo totale di un impianto. Gli andamenti e i valori dei punti di ottimo differiscono leggermente tra loro, principalmente perché gli input, soprattutto il rame in ingresso, appena estratto dalla miniera, sono quantificati diversamente tra i vari paradigmi. In più ogni metodo considera diverse categorie d'impatto; di conseguenza, anche se gli input avessero lo stesso contenuto exergetico, probabilmente non si sarebbero potuti ottenere risultati uguali, almeno per quanto riguarda il valore assoluto del consumo di risorse.

Un'anomalia che appare dal confronto tra risultati di CExC e TEC, è che sono pressappoco uguali, ma questo si può spiegare, dal fatto che in questo modello non vengono considerate risorse rinnovabili, per cui non si ha differenza nei termini considerati come input dei confini del sistema.

Dal lavoro svolto si può concludere che le risorse naturali sono di vitale importanza per la nostra società ed è necessario perseguire uno sviluppo che sia sostenibile. Quando si analizza il consumo di risorse naturali, l'exergia è la numeraria che bisogna scegliere; l'analisi dei processi è un buon approccio, che comporta alcune limitazioni, ad esempio, quando si posseggono dati incerti sulle filiere di produzione degli input al sistema considerato. Attualmente, più di una numeraria è impiegata nell'analisi di processo ma non si è riusciti ad identificare quale possa essere la migliore in assoluto. Bisogna ricordarsi che la termoeconomia è l'ambito in cui si opera quando si cerca di dare un senso economico ai risultati ottenuti tramite analisi termodinamiche; e che il costo exergetico è lo strumento che ha le potenzialità di legare questi due ambiti. Tra i paradigmi analizzati, si nota una certa somiglianza, ma non è facile capire quale possa essere quello da impiegare nel caso si voglia stimare il consumo di risorse. Poiché si sono ottenuti valori diversi sia per quanto riguarda il valore assoluto del consumo di risorse exergetiche, sia per ciò che concerne il valore dell'ottimo di funzionamento. Si propongono ulteriori studi e approfondimenti per capire quale paradigma va perseguito per avere una corretta misura del consumo delle analisi exergetiche.

Contents

List of Figures

List of Tables

Introduction

In the first half of the 20th century the human society has discovered so many technologies, mainly resource intensive [1], which have led our specie to an undisputed socio-economic development. To help this development grow and spread, natural resources had to be discovered and extracted at an always-higher pace [2].

During the second half of the 20th century human society started to understand that natural resources are finite and the environment needs to be taken into account in order to keep on going with the development [2].

Depletion or degradation of both renewable and non-renewable resources usually are not included in national accounts; strangely it happens that the economic well-being increases thanks to depletion of natural resources.[3]

The energy-containing resources have a relatively small value, for the consumer, while they are in their natural deposits. Additional energy is necessary to extract, transport and process them so they can be used. For some of these resources, like coal or oil, the 'energy to get energy' may not be identical to the one attained, and that could lead to the acceleration of depletion rate of total energy reserves [4].

Also the most concentrated mineral resources, which are being intensely exploited, are under scientific investigation, mostly concerning the processes of the mining industry. Moreover, due to the availability of these materials, fundamentals for a vast range of industries, governments have began to pay attention on this matter [5].

The beginning of the second millennium has been marked with a new concept of development for the human society, which is denoted as 'sustainable development'. In 1987, the World Commission on Environment and Development (WCED) defined sustainable development as "development that meets the needs of the present without compromising the ability of future generations to meet their own needs" [6].

The three factors included in a sustainable development vision are: industrial production (economic efficiency), equitable growth (social efficiency), and environmental protection. Among these factors, the latter is the major barrier in trying to accomplish the other two.[1]

The three factors are directly linked with three respective approaches, also showed in Figure 0.1:

- Economic
- Social
- Environmental

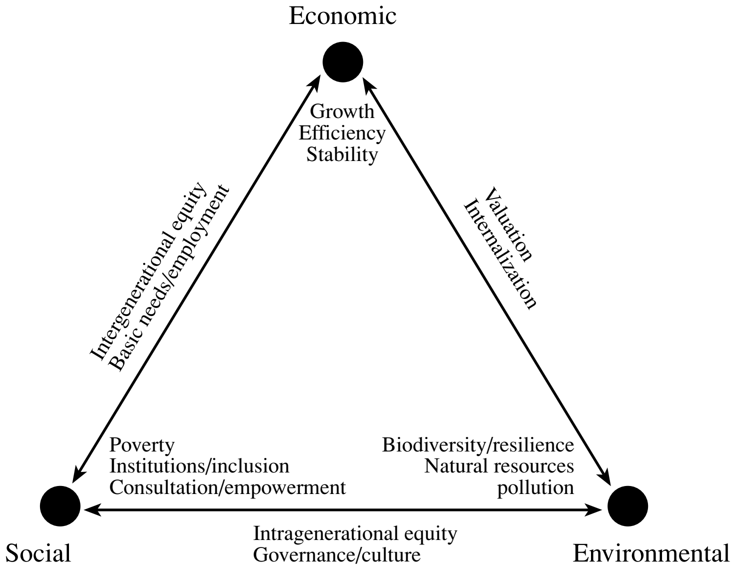

Figure 0.1 Three dimensions of sustainable development [7]

To achieve a sustainable development is a challenge for the entire world, and different policies have been proposed to pursue a sustainable path. The Millennium Development Goals (MDGs), which should be achieved within the year 2015, have been set by the United Nations. Recently the nexus between energy [6], water and food (mainly their access) and MDGs has become considerably manifest. In fact, starting from 2015 (Figure 0.2) there will be the Sustainable Development Goals (SDGs), created after the RIO+20 summit in Brazil in 2012. These six goals encompass both poverty eradication and protection of Earth's life-support system; below the list of goals, from [8]:

1. "**Thriving lives and livelihoods.** End poverty and improve well-being through access to education, employment and information, better health and housing, and reduced inequality while moving towards sustainable consumption and production;
2. **Sustainable food security.** End hunger and achieve long-term food security — including better nutrition — through sustainable systems of production, distribution and consumption;
3. **Sustainable water security.** Achieve universal access to clean water and basic sanitation, and ensure efficient allocation through integrated water- resource management;
4. **Universal clean energy.** Improve universal, affordable access to clean energy that minimizes local pollution and health impacts and mitigates global warming;

5. **Healthy and productive ecosystems.** Sustain biodiversity and ecosystem services through better management, valuation, measurement, conservation and restoration;
6. **Governance for sustainable societies.** Transform governance and institutions at all levels to address the other five sustainable development goals."

Despite of the SDGs, which are an improvement of the MDGs (Figure 0.2), 'sustainability' remains not easy to quantify and still many scientific researches try to comprehend how to do it rigorously. In accordance with the first five SDGs the present work explores different methodologies and approaches regarding natural resource consumption assessment.

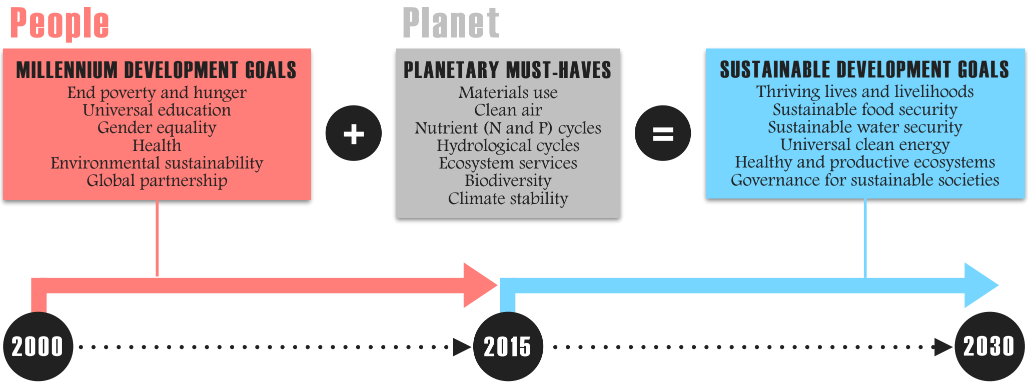

Figure 0.2 From the Millennium Development Goals to the Sustainable Development Goals (adapted from [8])

It will be showed how the scientific world tries to measure and compute natural resources, analysing different numeraires and, to each of them, a description of its process analysis application will correspond. Afterwards the main focus will be on exergy and exergy-based paradigms, within the thermoeconomics framework, for the computation of resource consumption.

1 Basic concepts

1.1 Definitions

1.1.1 Ecosystem

An ecosystem is defined as: "*a system involving the interactions between a community of living organisms in a particular area and its non-living environment*" [9]. The just cited 'interactions' can be called 'ecosystem functions', and they include such things as energy transfer, nutrient cycling, gas regulation, climate regulation, and the water cycle [10]. Since every ecosystem needs at least an external supply of energy, if not even matter, it comes natural saying that natural resources are essential to let ecosystem functions take place and for the sustainability of the system.

Going further into details, an ecosystem function that has value to human beings is called 'ecosystem service' [10]. Therefore, from a certain point of view, human beings can also be considered part of what is commonly referred to as natural ecosystem, since they are receiving the services. Admitting so, the natural resources, which are essential for the ecosystem, are the same resources that our society needs to survive.

1.1.2 Natural resources: stocks and flows

On a global scale the ecosystem has only solar energy flowing inside its boundaries, while the rest of the supply is mostly matter that can have either biotic or abiotic origins, and which corresponds to the Earth's natural resources, including solar energy. Every time a component of the ecosystem uses these resources it will produces wastes that other components could elaborate in order to meet their own needs.

Natural resources can be classified in two macro-categories: *flows* and *stocks* [11]. Among the first ones there are solar energy, wind energy and ocean currents; they have limited size but flow continually [11]. The second macro-category can be further subdivided, based on the time of reproduction, into *deposits* or *dead stocks* and *funds* or *living stocks*. The natural flows together with the flows from funds can be addressed as *renewable* flows. Deposits can also give origin to flows, but only if they are dispersed or depleted [11]. Look at Figure 1.1: deposits derive from the toxic matter that does not recirculate in the biosphere, like fossil fuels; while, with sunlight and nutritious matter, such as mineral substances, water, and carbon dioxide, the funds create biological matter that can be withdrawn without any stock decrease.

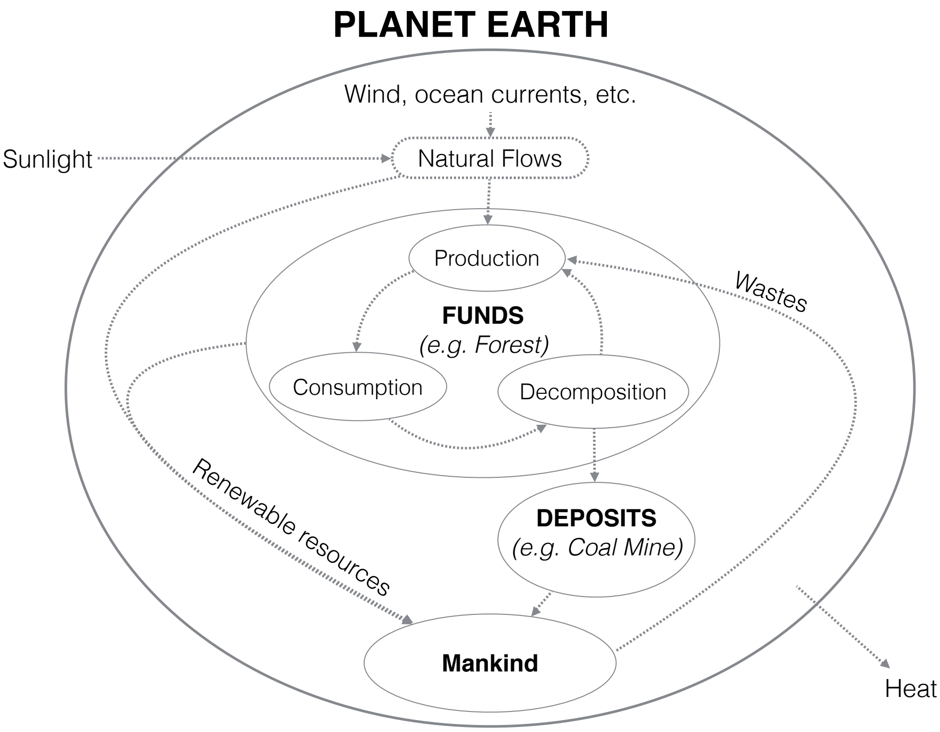

Figure 1.1 Schematic view of global ecosystem (adapted from [12]**)**

Just to make clarity on the terminology, in the economic fields the expression 'natural capital' embodies the land and the natural resources [13] that usually are evaluated on monetary basis. That means that economists seems to exclude deposits from what they call natural capital.

What the mankind has done so far, as an ecosystem's component, is to use natural resources for its own needs, producing wastes that other components of the global ecosystem are not able to elaborate, or at least not as fast as they are generated.

Finally, as part of the ecosystem, the mankind should think about what is required for its survival, but keeping in mind that it will always remain integral part of the natural global ecosystem.

1.1.3 Use, depletion and consumption

It is widely known that some of the natural resources are being consumed by human society, but in the last few decades the scientific society has started to worry about resource depletion [14]. But, when talking about natural resources, it is necessary to clarify the difference, as Reisemann says in [15], among the terms: use, consumption and depletion. The former, related to resources, stands for whenever these enter the technosphere and then leave it, or are stored within it. The second term has to be used if the energy or material flow is transformed inside the system, and there has been a change of its quality or quantity. The last term implies the decrease in quantity of material found in nature.

Reisemann [15] argues about how resource consumption can be measured, he gives a detailed list of different methodologies, which can assess the flows of matter and energy between the environment and the anthroposphere.

He also mentions three different definition of resource consumption in relation to three different views: the economist's view, the physicist's view and the ecologist's view. The economist considers anything that takes part to the production of goods and services. The physicist accounts only energy, material and information flows that could be transformed into anything useful. The latter, including all, but only, the natural resources, considers the "naturally occurring components of the environment that can sustain or benefit organisms, population, or communities within an ecosystem" [15].

Combining the last definitions, it can be written: "Resources are the flows and reservoirs of matter and energy that can sustain or benefit living system" [15].

Manmade and natural objects can be included, implying also that resources have a potential utility, in a sense that any resource can have a variety of different uses. Every time that a path to transform a resource is undertaken some of the possible uses are automatically excluded and so it can be said that the potential utility of the same resource decreases. Of course the number of possible paths for a resource are determined by the available technologies and human ingenuity. [15]

1.2 Facing natural resources depletion: economics versus natural sciences

When talking about resources consumption it bobs often up the issue about if the solution should be found through economics or natural sciences, like ecology and thermodynamics. The first, *neoclassical economics*, is the science of "allocation of scarce resources among competing ends" [16], which uses money as numeraire with no thermodynamic limitations. On the other side, ecology studies the distribution of plants and animals [17], while thermodynamics and its laws describe matter and energy flows [18]. Both ecology and thermodynamics use physical units, like mass or energy, as numeraire.

In 1975, sponsored by IFIAS (International Federation of Institutes for Advanced Study), twenty-seven economists and scientists attended a workshop called "Energy Analysis and Economics", where there was agreement on the fact that energy analysis could be utilized to help in the allocation of scarce energy resources [19]. Energy and economic analysis were discovered to be complementary, and also, energy analysis could help in setting the constraints to markets and the economic society.

To face the problem of natural resources depletion among the existing approaches, one could find thermoeconomics and ecological economics. The former represent "a thermodynamic approach to economics" [20], and it will be examined in this work; the latter "seeks to ground economic thinking in the dual realities and constraints of our biophysical and moral environments" [10].

In general, ecology and economics can be regarded as the two disciplines more concerned about sustainability [17]. On this view, Ecological **E**conomics (EE) tries not only to describe the world, but also proposes a way to make it better [10]. EE merges together the ecological vision of sustainability with the allocation rules of macroeconomics and microeconomics.

Thermoeconomics is mainly used in industrial processes, but its basic rules can be applied to solve some economic problems [20]. As Valero [21] pointed out the word thermoeconomics "suggest the transition between thermodynamics and economics".

1.3 How to measure natural resources

When it comes to measure natural resources, there is not a unique measurement unit, and it is difficult to establish the only one unit that could fit, because it depends on the scope a certain resource will be used for. The following numeraire are going to be described in this section:

- Mass
- Energy
- Entropy
- Exergy.

Think of, for example, a deposit of coal or copper, it can be easily described using the number of tonnes of material contained into it. Also in case of extraction of natural resources the amount of mass flowing out a mine can be a useful data.

Also volume can be used as measurement unit, because it gives us the perception of the space that is filled by the mentioned resources, and it applies perfectly when fluids are involved, like water, or oil or natural gas. Using density, mass can be easily converted into volume, and the opposite, without changing the information bore in it.

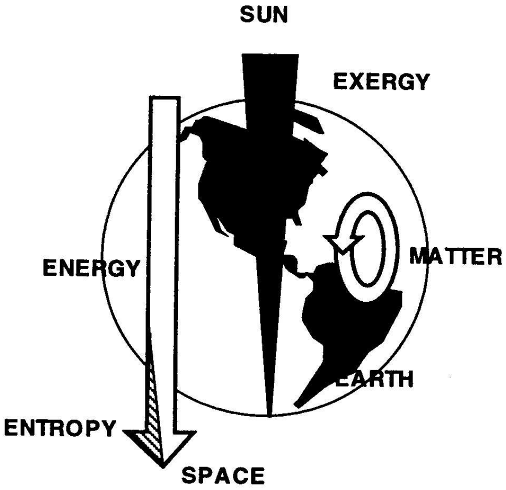

Figure 1.2 Schematic view of numeraire flows into and through the Earth [22]

Since a relevant percentage of natural assets are mainly used for energetic purposes, the *energy* content of these particular resources is privileged in respect to others numeraire when measurements have to be done.

As said before, from the usage of a resource depends the unit to measure it. Some units can express not only the physical quantity but also the 'quality' of the resources, like when terms such as *entropy* or *exergy* are used. Further explanations will follow next.

1.3.1 Mass

Mass is an extensive thermodynamic variable. It is directly related to the material quantity of a substance in a thermodynamic system, it is easy to measure and accessible to the senses [23].

1.3.2 Energy

1.3.2.1 Definition

'Energy' can be defined as "the ability of a system to cause change and, more specifically, to perform work" [24]. Energy is an extensive variable of a thermodynamic system, but it cannot be measured directly and it is not directly accessible to human senses [23]. Actually it is the energy 'flowing' the considered characteristic instead of its 'content', with Joule (J) as its measurement unit [24].

Taking into consideration an isolated system, its total energy content cannot change, and the reason stands in the "First Law": 'energy is conserved'. So energy can be only transformed or converted from a kind to another. Potential energy, kinetic energy, heat, mechanical work, chemical energy, these are some forms of energy that a system can contain.[23]

When the word *heat* is used in thermodynamics it is referred to kinetic energy of molecular motion, and with the term internal energy both heat and chemical energy are embraced. [23]

1.3.2.2 Calculation

'Enthalpy' is the term that measures the total energy content of a system [23]. Enthalpy (H) encompasses both potential work associated with pressure ($p{\cdot}V$) and the internal energy (U).

$$H = U + p{\cdot}V \tag{1.1}$$

Therefore, defined the control volume of a system, its matter embodies the enthalpy that represents its total energy.

In case a chemical reaction happens (e.g. '$A + B \rightarrow C + D$'), the released or absorbed heat can be addressed as the chemical energy embodied in the reactants. For fuels combustion, the released heat is a change of enthalpy and it is called heat of combustion.

In general, enthalpy can be considered as a measure of energy according to the first law, but it doesn't reflect the quality of energy [23].

The measure of the potential of energy resources to release heat or perform work is defined as 'free energy', which is *numerically similar* to their enthalpy [4].

1.3.2.3 Applications

Energy has been used as environmental impact indicator after the 1970s, because of the oil crisis, and again after the 1990s for the greenhouse implications of burning fossil fuels [25].

1.3.3 Entropy and entropy generation

1.3.3.1 Definition

As affirmed in section 1.3.2, the conversion of heat into work is constrained by fundamental limits, which are regulated by the Second Law of thermodynamics: "in any transfer or conversion of energy within a closed system, the entropy of the system increases" [26].

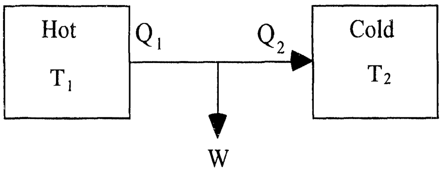

Figure 1.3 Illustration of the observation made by Carnot [27]

After Carnot, Clausius [28], in 1865, introduced the variable entropy (S),Carnot, in 1824, was the first in setting those limits after finding a general expression for the maximum amount of work extractable from heat using an engine that operates between two bodies at different temperatures [27].
If the cold body is the environment, those limits are linked only to the temperature of the hot body. So, the higher is the temperature the higher will be the limit and, therefore, bigger will be the amount of work that can be obtained. More in general, the bigger is the temperature difference between heat source and sink the bigger will be the conversion efficiency η . [23]

$$\eta = 1 - \frac{T_2}{T_1} \tag{1.2}$$

Carnot's Principle states: "No heat engine ***E*** can be more efficient than a reversible one $\boldsymbol{E_r}$ operating between the same temperatures". [29]
defined, 'in a no intuitive way' [23], as the sum of heat supplied divided by its temperature. The entropy increment of a system, which is supplied with a small quantity of heat, is [30]:

$$dS = \frac{dQ}{T} \tag{1.3}$$

Where dQ is the incremental heat flow and T is the absolute temperature of the system. In integral form [29]:

$$\Delta S = S_A - S_B = \int_B^A \frac{dQ}{T} \tag{1.4}$$

Where 'A' and 'B' are respectively the final and the initial thermodynamic status of the system. If one pursues the process backward ('A→B') will result:

$$\int_A^B \frac{dQ}{T} \leq S_B - S_A \tag{1.5}$$

Which means [29]

$$S_A \geq S_B \tag{1.6}$$

Another formulation, called 'Clausius inequality' [27], can be used to express the concept of (1.6)

$$dS \geq \frac{dQ}{T} \tag{1.7}$$

Which also includes the limit case of (1.3) and confirms the Second Law. Whilst the 'Clausius theorem' [31] states that the final entropy of a system equals its initial entropy after a reversible cycle, in formula

$$\oint \frac{dQ}{T} = 0 \tag{1.8}$$

Any system in thermodynamic equilibrium has unique entropy, and, for non-equilibrium processes in an isolated system, it cannot decrease [32]. The equilibrium of a system is found when there are no gradients within it [24]. Ayres et al. [23] affirmed that "since any closed system must eventually reach a static equilibrium state in which all forces are balanced and 'nothing happens or can happen', it follows that such state corresponds to maximum entropy".

Dincer and Cengel [26] highlighted that:

- Entropy measures the molecular disorder within a system;
- Entropy cannot be destroyed, only generated;
- Energy exchanges across a system boundary increase or decrease the entropy of the system.

In addition, the *third law of thermodynamics*, formulated by Nernst, states that "at the absolute zero of temperature the entropy of every chemically homogeneous solid or liquid body has a zero value"[27], in symbols:

$$T \to 0 \text{ K} \;\Rightarrow\; S \to 0 \tag{1.9}$$

According to (1.9) an absolute value for entropy exists.

In addition, in 1909, Carathéodory demonstrated that "a necessary consequence of the property of irreversibility per se is the existence of a non-decreasing function of the independent state variables" [23].

The potential entropy, or 'entropy generation', ΔS of a system is determined by the difference between the entropy value reached by a system, after it has reached the thermal and molecular equilibrium (S_{td}), and the entropy value of the system at the beginning of measurements (S_t).

$$\Delta S = S_{td} - S_t \tag{1.10}$$

Entropy generation can measure the extent to which energy becomes unavailable during a process [23].

1.3.3.2 *Statistical interpretation of entropy*

"Entropy is a well defined and mathematically precise monotonic indicator of order" [33].

Boltzmann proposed the following formulation of entropy [27]

$$S = k_B \ln W \tag{1.11}$$

where k_B is the Boltzmann constant (k_B=1.381· 10^{-23} J/K), W (or 'Ω' [33]) is the number of microstates corresponding to the macro-state whose entropy is *S*. In a box (Figure 1.4) half-filled by N_1 molecules of a gas, and with N_2 molecules of the same gas on the other half, the term W results [27]

$$W = \frac{(N_1 + N_2)!}{N_1!N_2!} \tag{1.12}$$

"The entropy of the state of a system is a measure of the probability of its occurrence" [26]. A state of low probability has low entropy; a state of high probability has high entropy. For this reason, energy transfers are spontaneous from a hot body, high entropy, to cold one, respectively lower entropy [26].

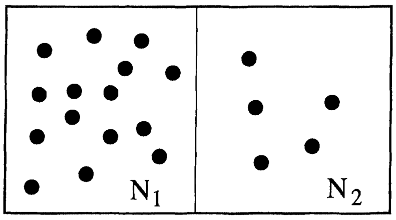

Figure 1.4 Box containing a gas made of (N_1+N_2) molecules [27]

1.3.3.3 Calculation

System balance

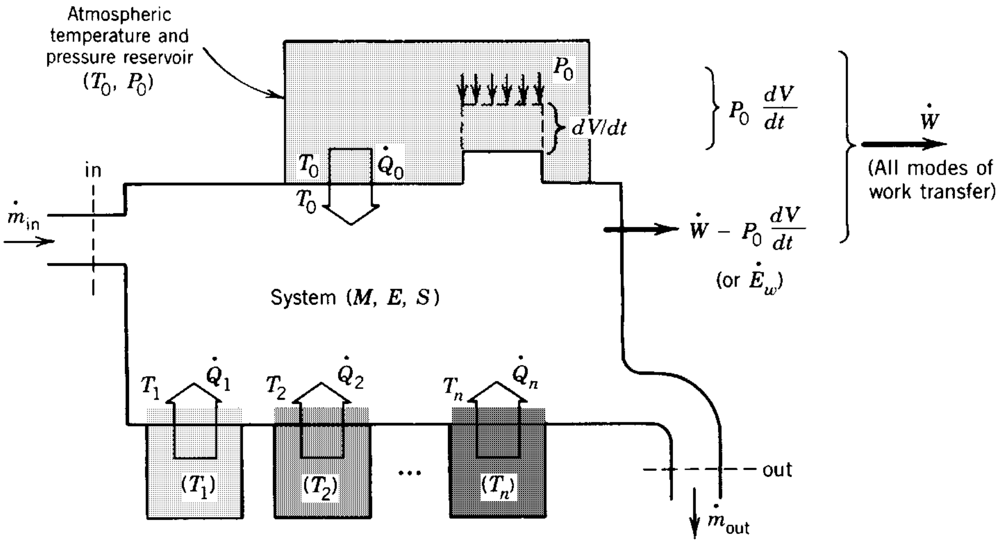

Figure 1.5 General work transfer, heat transfer, and mass flows between a system and its environment in the unsteady state [34]

Consider a system-environment configuration, like the one shown in Figure 1.5, which operates in the unsteady state [34]. The energy balance (1.13) can be written, followed by the entropy balance (1.14).

$$\frac{dE}{dt} = \sum_{i=0}^{n} \dot{Q}_i - \dot{W} + \sum_{\text{in}} \dot{m}h^\circ - \sum_{\text{out}} \dot{m}h^\circ \qquad (1.13)$$

$$\dot{S}_{gen} = \frac{dS}{dt} - \sum_{i=0}^{n} \frac{\dot{Q}_i}{T_i} - \sum_{\text{in}} \dot{m}s + \sum_{\text{out}} \dot{m}s \geq 0 \qquad (1.14)$$

Where:

- $\dot{Q}_i$ is the heat transfer rate coming from a temperature reservoir T ;
- $\dot{W}$ is the net work transfer rate;
- $\dot{m}_{\text{in}}$ and $\dot{m}_{\text{out}}$ are the mass flow rates respectively through inlet and outlet;
- note that, h^0 is the notation, used by Bejan [34], to indicate the sum of specific enthalpy, kinetic energy, and potential energy of a particular stream at the boundary;
- $\dot{S}_{\text{gen}}$ is the entropy generation.

It is demonstrated, in [34], that the lost power is

$$\dot{W}_{\mathrm{rev}} - \dot{W} = T_0 \dot{S}_{\mathrm{gen}} \tag{1.15}$$

where $\dot{W}_{\mathrm{rev}}$ stands for the net reversible work transfer rate. Equation (1.15) is known as the Gouy-Stodola theorem [34].

If one denotes the entropy of a system by S_{sys}, the system's entropy change would be

$$\Delta S_{sys} = \Delta_e S_{sys} + \Delta_i S_{sys} \tag{1.16}$$

Where $\Delta_i S_{sys}$ is the entropy produced inside the system and $\Delta_e S_{sys}$ is the entropy exchange between the system and the environment [35]. Focusing on the former, since any real transformation that takes place inside the system generates some irreversibility [15], it follows that

$$\Delta_i S_{sys} > 0 \tag{1.17}$$

If the system is made of two or more subsystems, then the entropy of each subsystem can either increase or decrease, but their sum will always increase.

Formulation of typical entropic generations

Mixing various gas flows result into an increase of total entropy of the flows [36], which is

$$\Delta S_{mix} = -R \sum_i n_i \ln y_i \tag{1.18}$$

where R is the gas constant, n_i is the mole number of substance *i* and y_i is the respective mole fraction in the mixture.

In combustion reaction the entropy change [36] is

$$\Delta S_{comb} = \Delta S_r^0 + \int_{T_0}^{T_f} \frac{C_p(T)\,dT}{T} \tag{1.19}$$

where $C_p(T)$ is the heat capacity of the reaction products, T_f is the adiabatic flame temperature, and the ΔS_r^0 is the entropy change related standard state (p_0=101325 Pa, T_0=298 K [37]). If combustion of a fuel is executed, the heat generated will decrease its capability to perform mechanical work with the diminishing of temperature. For this reason, and looking at (1.19) and (1.3), entropy will increase.

The differential entropy change for arbitrary chemical reactions at constant pressure [27] is

$$dS_{ch} = \frac{dH}{T} - \frac{\sum \mu_k d_e N_k}{T} - \frac{\sum \mu_k d_i N_k}{T} \tag{1.20}$$

with μ_k being the chemical potential of species *k*, and d_eN_k and d_iN_k being the change in mole number of species k due to, respectively, exchange with the environment and to internal reactions.

The transfer of heat, that ends with space heating, is a main entropy generation mechanism [36], the 'useful' entropy production ΔS_{th} can be computed as

$$\Delta S_{th} = q\left(\frac{1}{T_0} - \frac{1}{T}\right) \tag{1.21}$$

where *q* is the transferred heat, coming from the inside of the system, *T* is the system temperature, and T_0 is the environment temperature.

When there is phase transformation the entropy change is [36]:

$$\Delta S_{pt} = \frac{\Delta Q_{pt}}{T_{pt}} \tag{1.22}$$

with ΔQ_{pt} being 'the latent heat' [27] absorbed at the fixed temperature of phase transformation T_{pt}.

In case an electric cable is considered [27], the total entropy production rate is

$$\frac{dS}{dt} = \frac{VI}{T} \tag{1.23}$$

where *VI* is called 'ohmic heat' and is the product of potential difference and current, representing the heat generation rate, while T is the temperature.

1.3.3.4 Applications

If resources have to be considered, when a natural resource embodies potential energy, that can be transformed into mechanical work and it is regarded as ‘a potential source of future entropy increase’ [23]. So, when a system is not in equilibrium with the environment, the difference between its actual entropy and its future entropy, after the equilibrium, is the measure of its potential for performing work in future.

“Thus entropy content cannot be used for evaluating the absolute utility of a resource; entropy production only accounts for changes in utility” [15]. According to the last part of the previous affirmation, ‘entropy production’, or ‘entropy generation’, can be useful as a proxy to measure real consumption covering the physical aspects of transformations. When a physical resource is consumed, its potential utility decreases. The ‘potential utility’ corresponds to “the size of the set of all possible uses of a given amount of resources” (Figure 1.6). The actual usefulness of a resource is strictly “dependent on the preferences, abilities, and circumstances of the respective user”. [15]

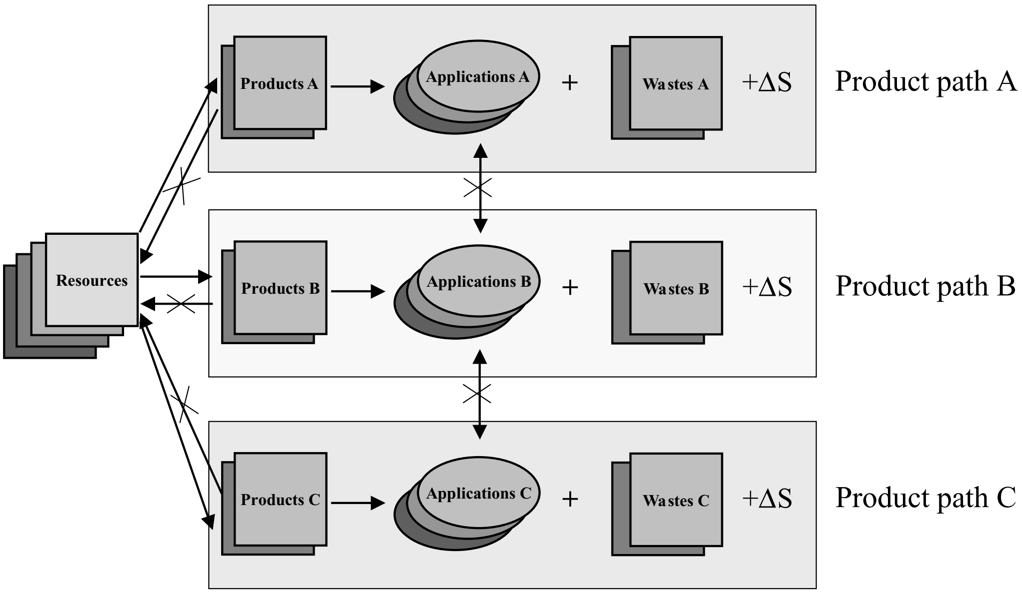

Figure 1.6 When resources are consumed in a process the actual set of possible uses decreases. The size of this set can be viewed as the potential utility of these resources. [15]

Gößlin-Reisemann proposes to measure resource consumption by measuring the actual loss of potential utility, which is reflected by the irreversibility of a process. Therefore, considering an open system combined with its surrounding environment, and because of the second law of thermodynamics entropy increase is directly related to irreversibility, entropy can be used [15].

In [35], Goßling-Reisemann states that *“entropy generation does not measure the consumption of only one resource. Instead all resources are considered together and the overall consumption of resources is assessed”.*

This last affirmation can be reinterpreted as: when entropy generation analyses are performed the system has to be considered in its completeness and entirety, taking into account all parts of the system including, especially, its boundaries and surroundings.

Entropy production considers all resources together [15]. Entropy cannot be directly measured but only derived, using formulae, from other measurable thermodynamic variables. [23]

1.3.4 Exergy

1.3.4.1 Definition

The term 'exergy' is used to express the degradation of energy in conversion processes [38]. In works of the last half century, instead of exergy it can be found, [39]:

- available work
- availability
- available energy
- useful energy
- potential work
- potential entropy.

All the mentioned terms would embody the significance that Gibbs attributed to his 'free energy' in 1878 [40].

Exergy can be described as *"the amount of useful work extractable from a generic system S when it is brought to equilibrium with its reference environment E through a series of reversible processes in which the system can only interact with such environment"* [41]. As a matter of fact, Dincer and Cengel [26] describe exergy as a 'co-property' of a system and the reference environment, instead of a simple thermodynamic property.

Whenever irreversibilities occur within a process destruction of exergy happens [26].

1.3.4.2 Calculation

For an open system, like in Figure 1.7, the 'exergy balance' (1.24) can be written using energy and entropy balances.

$$\frac{d\mathbf{B}}{dt} = \sum_{l=1}^{p}\left(\dot{\mathbf{B}}_{\mathrm{Q}}\right)_l - \dot{\mathbf{B}}_{\mathrm{W}} + \sum_{j=1}^{q}\left(\dot{\mathrm{m}}\cdot\mathbf{b}_{\mathrm{M}}\right)_j - \sum_{k=1}^{r}\left(\dot{\mathrm{m}}\cdot\mathbf{b}_{\mathrm{M}}\right)_k - \dot{\mathbf{B}}_{\mathrm{des}} \tag{1.24}$$

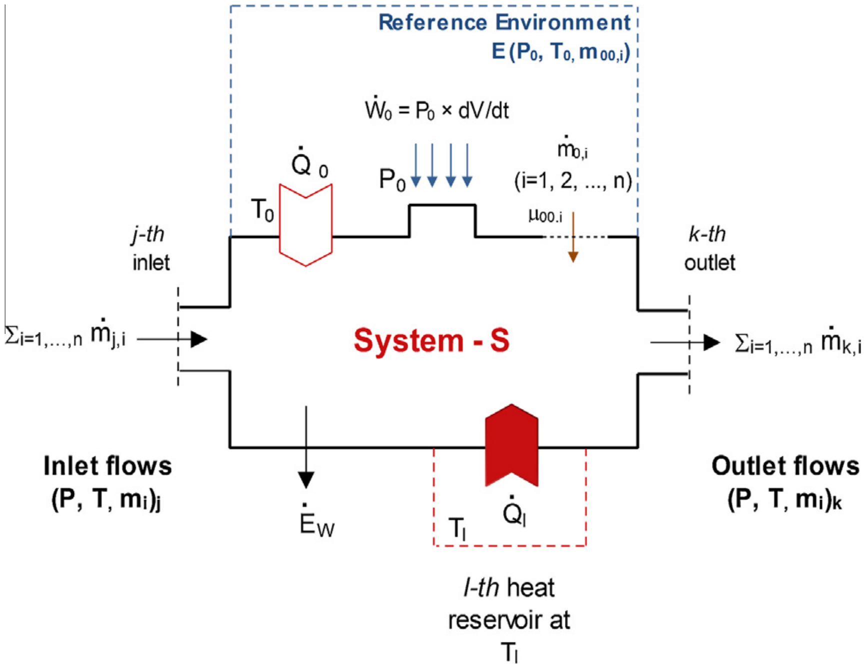

Figure 1.7 Control volume for exergy balance [38]

Actually it is not appropriate talking about 'balance', because the term $\dot{\mathbf{B}}_{\mathrm{des}}$, in (1.24), represents only the missed quantity that helps closing the exergy balance [38]. This is because exergy, like entropy, is not conserved, and for that reason would be better talking about 'exergy accounting' [38].

The terms of (1.24) are following described with the notation proposed by Kotas [42].

The specific exergy of a stream of matter, made of *n* components, $\mathbf{b}_{\mathrm{M}}$ is:

$$\begin{aligned}\mathbf{b}_{\mathrm{M}} &= g(z_1 - z_0) + \frac{1}{2}\left(V_1^2 - V_0^2\right) + (u_1 - u_0) + P_0(v_1 - v_0) \\ &- T_0(s_1 - s_0) + \frac{1}{MM_{mix}} \sum_{i=1}^{n} \left(\mu_{i,0} - \mu_{i,00}\right) x_i\end{aligned} \tag{1.25}$$

where the first and the second terms in (1.25) are respectively potential and kinetic energy, which can be entirely converted into work:

$$\mathbf{b}_{\mathrm{pt}} = g(z_1 - z_0) \tag{1.26}$$

$$\mathbf{b}_{\mathrm{kn}} = \frac{1}{2}\left(V_1^2 - V_0^2\right) \tag{1.27}$$

The last addendum in (1.25) is the *chemical* exergy:

$$\mathbf{b}_{\mathrm{ch}} = \frac{1}{MM_{mix}} \sum_{i=1}^{n} \left(\mu_{i,0} - \mu_{i,00} \right) x_i \tag{1.28}$$

While the *physical* exergy is:

$$\mathbf{b}_{\mathrm{ph}} = \left(u_1 - u_0 \right) + P_0 \left(v_1 - v_0 \right) - T_0 \left(s_1 - s_0 \right) \tag{1.29}$$

Combining (1.25) with (1.26), (1.27), (1.28) and (1.29), it becomes:

$$\mathbf{b}_{\mathrm{M}} = \mathbf{b}_{\mathrm{pt}} + \mathbf{b}_{\mathrm{kn}} + \mathbf{b}_{\mathrm{ph}} + \mathbf{b}_{\mathrm{ch}} \tag{1.30}$$

with the subscript '00' the *Dead state* is intended, which is the status where the system is both in thermo-mechanical and chemical equilibrium. While subscript '0' represent the *Environmental state*, in which only thermo-mechanical equilibrium is reached [38].
The other terms in (1.24) symbolize the *immaterial* interactions: exergy transfer associated with heat and work transfers through system boundaries [38]:

$$\dot{\mathbf{B}}_{\mathrm{Q}} = \dot{Q} \cdot \left(1 - \frac{T_0}{T} \right) \tag{1.31}$$

$$\dot{\mathbf{B}}_{\mathrm{W}} = \dot{W} - P_0 \frac{dV}{dt} \tag{1.32}$$

Then the exergy destruction corresponds to the irreversibilities within the system boundaries [43], like in Gouy-Stodola theorem (1.15), as so:

$$\dot{\mathbf{B}}_{\mathrm{des}} = T_0 \cdot \dot{S}_{irr} \tag{1.33}$$

Reference environment

To calculate the exergy of any natural resource a definition of reference environment (R.E.) is required [44]. One possible definition of R.E. can be: "a system of unspecified dimensions in a perfect thermodynamic equilibrium. Within the reference environment there are no gradients of temperature, pressure, chemical composition, kinetic energy and potential energy: hence it is impossible to produce work through interaction between two or more portions of the same environment" [42].

The natural environment cannot be the reference environment, because its intensive properties vary temporally and spatially [26]. Moreover the natural environment has a non-zero exergy.

Two are the main categories of R.E. [45]: 'partial' and 'comprehensive'. The first one is related to the process and its limitations, the second one is more appropriate "to evaluate the natural capital on Earth [45].

The most significant reference environment models proposals, from [26], are reported below:

- *Natural–Environment–Subsystem model* — T_0=25°C, p_0=1 atm, fixed chemical composition of moist air (N_2, O_2, H_2O, Ar, CO_2, H_2) in equilibrium with condensed phases (Water, Limestone and Gypsum);
- *Reference–Substance model* — a substance is selected for each chemical element and assigned zero exergy;
- *Equilibrium and constrained–equilibrium model* — all materials present in atmosphere, oceans and in a layer of the crust of the earth, which thickness has to be defined of, are combined together and for a temperature of 25°C an equilibrium composition is calculated;
- *Process–dependent model* — contains only the components of the considered process, which the model is dependent of, at temperature and pressure of the natural environment [46].

Szargut et al. [45] proposed to formulate a unique reference environment (*R.E.*), which should have the following characteristics:

- in its proposal Szargut makes use of the 'Earth similarity criterion', which states: "if the stability of the possible different reference substances for a specific element is within a certain threshold, then the most abundant Reference Substance will be chosen";
- Szargut's dead environment is similar to the real physical environment;
- if a R.E. considers a crust thickness bigger than 0.1 m and an ocean's depth bigger than 100 m it would be too different from the real Earth;
- reference substances are assumed to be the free chemical elements present in the atmospheric air (O_2, N_2, Ar, He, Ne, Kr, Xe) and the compounds H_2O, CO_2 .

Exergy to energy conversion factors

In order to understand the numerical relevance of exergy in respect to some energy forms, in Table 1-1, it has been reported some 'exergy factor', which is the ratio between exergy and energy for any form of energy.

Table 1-1 Exergy factors corresponding different forms of energy (from Wall 2009 [47]**)**

	Form of energy	Quality index (Exergy factor)
Extra superior	Potential energy[1]	1
	Kinetic energy[2]	1
	Electrical energy	1
Superior	Nuclear energy[3]	about 0.95
	Sunlight	0.93
	Chemical energy[4]	about 1
	Hot steam	0.6
	District heating	0.3
Inferior	Waste heat	0.05
Valueless	Heat radiation from the earth	0

[1] e.g. highly situated water resources

[2] e.g. waterfalls

[3] e.g. the energy in nuclear fuel

[4] e.g. oil, coal, gas or peat

Exergy of materials

"The thermodynamic value of a mineral could be defined as the minimal work necessary to produce the mineral with a specific structure and concentration from materials in the environment"[44].

A mineral deposit possesses a concentration of mineral that is higher than its surrounding environment (Figure 1.8). When the mineral is mined the exergy content of the mineral is preserved, but when it is enriched the exergy content increases. And finally "when a concentrated mineral is dispersed, its exergy content is decreased"[26].

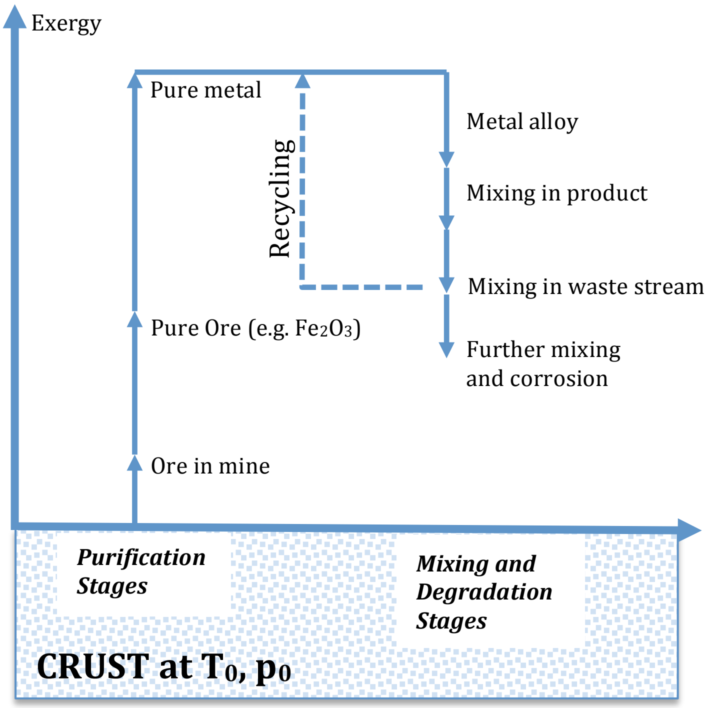

Figure 1.8 Theoretical exergy values for a metal extracted from the Earth's crust shown at various stages of a product life cycle (adapted from [35])

The standard chemical exergy of any chemical compound can be obtained through the exergy balance of a reversible formation reaction [45], viz

$$b_{ch\ n} = \Delta G_f + \sum_e n_e b_{ch\ n\ e} \tag{1.34}$$

where ΔG_f is the formation Gibbs energy, n_e is the amount of kmol of the element *e*, and $b_{ch\ n\ e}$ is the standard chemical exergy of the element *e*.
In case of a gaseous substance their standard exergy results

$$b_{ch\ n} = -RT_0 \ln \frac{p_{0n}}{p_n} \tag{1.35}$$

Where R is the gas constant, T_0 is the standard temperature (298,15 K), p_{0n} is the mean ideal gas partial pressure in atmosphere, and p_n is the standard pressure (101325 Pa). [45]
For solid substances the standard exergy results

$$b_{ch\ i} = -RT_0 \ln\left(\frac{n_{0i} c_i M_0}{l_i}\right) \tag{1.36}$$

where:

- n_{0i} is the mean molar concentration of the i-th element in the continental part of the Earth's crust,
- l_i is the number of the atoms of i-th element in the molecule of the reference species,
- c_i is the fraction of the i-th element appearing on the form of reference species, and
- M_0 is the mean molecular mass of the upper layer of the continental part of Earth's crust.[45]

For the sake of completeness the exergy of species dissolved in seawater is

$$b^0_{ch\ el} = j\left[-\Delta G^0_{f\ ref} + \frac{1}{2} z b^0_{ch,H_2} - \sum v_k b^0_{ch,el-k} - 2.303 RT_n z(pH) - RT_n \ln m_n \gamma\right] \tag{1.37}$$

where:

- j is the number of reference ion molecules derived from one molecule of the element under consideration;
- $\Delta G^0_{f\ ref}$ is the standard normal free energy of formation of the reference species;
- z is the number of the elementary positive charges in the reference ion;
- v_k is the number of molecules of additional elements in the molecules of the reference species;
- b^0_{ch,H_2} and $b^0_{ch,el-k}$ are standard chemical exergies of hydrogen gas and of the *k*th additional element, respectively;
- m_n is the conventional standard molarity of the reference species in seawater,
- γ is the activity coefficient (molarity scale) of the reference species in seawater; and
- pH (=8.1) is the pH of seawater.[44]

1.3.4.3 *Applications*

Exergy is stored in resources in the form of chemical, thermal, kinetic, potential, nuclear and radiative energy. The assignment of the adequate type of exergy depends on resource use:

- Chemical exergy is applied on all material resources, for biomass, water and fossil fuels (i.e. all materials that are not reference species in the reference state)
- Thermal exergy is applied for geothermy, where heat is withdrawn without matter extraction
- Kinetic exergy is applied on the kinetic energy in wind used to drive a wind generator
- Potential exergy is applied on potential energy in water used to run a hydroelectric plant
- Nuclear exergy is applied on nuclear fuel consumed in fission reactions
- Radiative exergy is applied on solar radiation impinging on solar panels.

For instance, noise could also include kinetic energy, but it is not considered as a useful resource. [48]

Initially, exergy was mainly used to analyse industrial system performances [49]. Now exergy is considered a “primary tool” for measuring the impact on the environment of energy resource utilization [26]. Later in this work will be described that exergy can also be related to environmental impact of emissions or to quantification of processes sustainability. And combining exergy-based method with Life Cycle Assessment (LCA) allows measuring equally all types of material and energy streams. [50]

1.3.5 Numeraire application comparison analysis

Resuming, mass, as a unit of account in the resource consumption framework, helps in giving the perception of quantity but lacks on the differentiation between distinct forms of natural assets, and mainly the ones with energetic scopes. Energy is certainly more than a step ahead of mass, because it can differentiate between energetic and non-energetic resources, measuring how much work can be obtained from a certain quantity of matter; but it is still lacking on giving information about the quality of the available resource. Entropy and exergy are similar on this last point and also comply with all the others. Nevertheless, in the literature has been found that exergy is a better measure of entropy in evaluating resource consumption for various reasons:

- exergy is more intuitive than entropy [23]
- defining a unique reference environment exergy can possess a baseline like entropy (Third Law of Thermodynamics)
- exergy can include mass, energy and also entropy when defining a matter stream
- exergy can directly measure the materials from their extraction

- few scientific papers address entropy as an indicator for resource consumption, while the word ‘exergy’ is often founded with the terms ‘resource consumption’ , ‘resource accounting’ and even ‘sustainable development’
- even the European Commission recommends that exergy should be used as indicator to assess natural resource depletion, since exergy methods are “based on an inherent property of a resource” [51]

As a consequence, it can be affirmed that, whenever resource consumption is the issue exergy should be used. And sometimes, exergy can be addressed as an interdisciplinary character in which three topics (as shown in Figure 1.9) can merge: energy, environment and sustainable development [26].

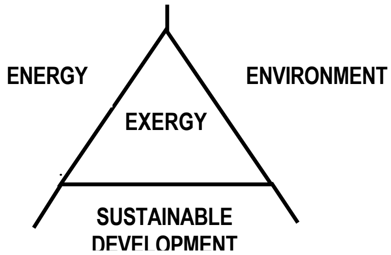

Figure 1.9 The interdisciplinary triangle of exergy [26]

2 Process analysis for natural resources consumption

It has been previously stressed how important natural resources are for the entire ecosystem. Since minerals and fossil fuels depletion is fundamental for our economy's sustainability [15], their evaluation has, and probably will, affect our society's development in the future.

The most relevant issue here is about measure the amount of resources extracted due to an increasing and always more globalized consumption. A part from the unit of account used, the boundaries of the analysed system should go upstream in all the processes, until they reach the natural deposits and funds.

Two are the main paths analysts can undertake to assess resources consumption:

- Process analysis;
- Input-output analysis.

The second approach will not be exploited in this work, but it is important to know that it can be mixed with the process approach to create various hybrid approaches, which are still not so diffuse in life cycle assessments.

2.1 Process analysis methodology

2.1.1 Definition

A process analysis studies the inputs and outputs to systems, and, using a numeraire, assigns to the product flows a numeric value. [52]

Chosen a numeraire for the process inputs, process analysis helps in the determination of total cost of 'direct' and 'indirect' resource requirements to obtain a desired output [53]. To be clear, the 'indirect' requirements equal the resources consumed in the processes, which generate the inputs not directly measurable with the chosen unit of account [54].

2.1.2 Methodology description

At first, when performing a process analysis, it is important to identify one particular product, either good or service, as the object of study [55]; right after that, the focus must go on the industry that produce the designated object, trying to figure out what goods and services are necessary in its manufacturing process [55].

A good way to understand how process analyses shall be performed, can be to follow the four steps highlighted by Treloar in [52]:

1. Measuring the direct exergy[1] (or energy, or mass, or entropy) requirements of the process;
2. Measuring the output of the process;
3. Quantifying the products directly required by the process; and
4. Applying first and third steps to the products quantified in the third step.

At first glance, the first and the second step can be viewed as a pure exergy (or energy, or mass, or entropy) based analysis, where all the inputs (step 1) have to be identified. But in details these two steps need to be seen separately as they appear already in the above list.

Among all the inputs only a portion can be expressed directly with the chosen numeraire, so they are determined within the first step. The second step needs to identify the unit of output desired. To do so, one has to consider the average production, taking measurements over a considerable period of time. After the firsts two steps the ‘direct exergy (or energy, or mass, or entropy generation) intensity’ can be obtained, which corresponds to the amount of unit of account directly consumed per unit of output.

If other products are included in the production process, they have to be quantified in the third step. Taking as an example an assembly line, there are a lot of material parts coming into the process, and a relatively small amount of direct energy is used to assemble them. But to produce those components, surely, some energy has been directly consumed: it could be past transformations or could be just their transportation from the warehouse to the assembly line.

It can be obvious, but just to be clear, also direct exergy (or energy, or mass, or entropy generation) of the first step has to be considered as an input together with the non-exergy products quantified in third step. Hence, the penultimate step begins to examine the process upstream and, it is immediately followed by the fourth step, where indirect exergy (or energy, or mass, or entropy generation) and ‘indirect’ products are going to be identified.

In Figure 2.1, there is a generic scheme showing how to consider the inputs when performing process analysis. From this view it should be simple understanding how to act when willing to go upstream, in order to reach all the primary inputs measurable with the same numeraire. It seems quite clear that this representation is applicable to any kind of process.

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[1] *Exergy* is mentioned first because it is the numeraire discussed the most in this work, but any unit of account could be used instead.

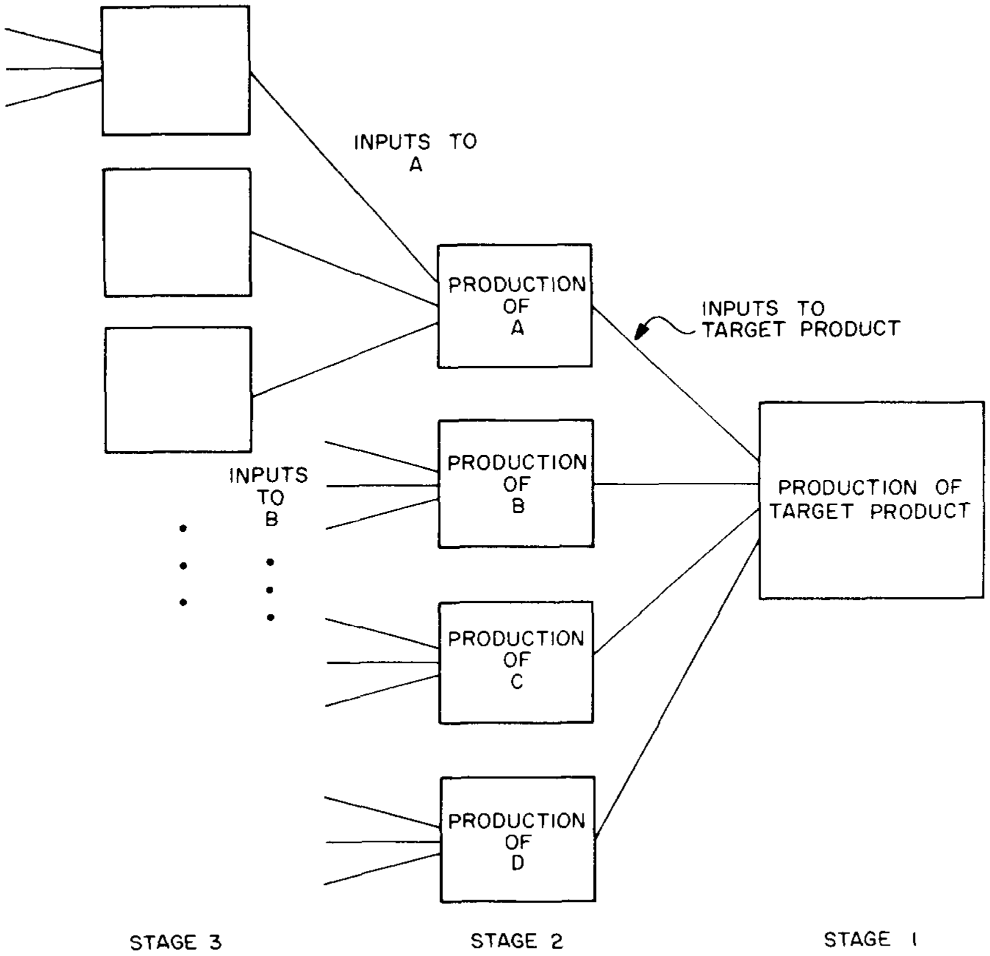


Figure 2.1 Successive stages in a process analysis [55]

Still referring to Figure 2.1, if energy were chosen as numeraire, one of the four inputs would represent the *direct energy* requirement, for example the output of 'PRODUCTION OF A' in the second stage. While, for the remaining three inputs, their energy supply has to be considered and summed up, so as to obtain the *indirect energy* requirements [55]. This last step shall be repeated until one reaches the interface between the technosphere and the natural environment.

To perform a process analysis it is required a wide amount of data on the production of the target product and on all the other inputs, not truncated [55]. Since a firm is usually part of a production sector, data are obtained from national statistics. If the production is singular, data must be collected directly from the manufacturer, or from consultants [55].

2.1.2.1 *A simple example*

At this point it seems necessary a numeric example, so to try eliminating any doubt on the topic of process analysis. The case reported is the one used by Bullard in his works, [3, 5].

In this example it is calculated the total energy embodied in cars, in a simple 3-sector economy, where each sector produces:

- Energy (measured in kJ),
- Cars, and
- All other goods or services (measured in €).

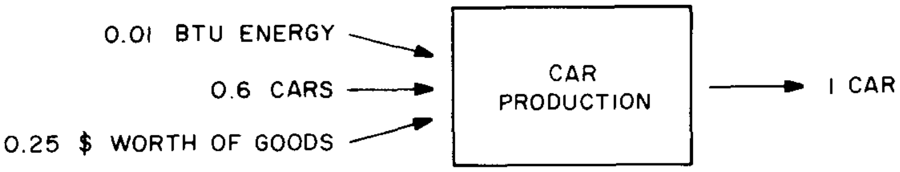


Figure 2.2 Production of cars [5]

From statistics, the car industry uses 0.6 car, 0.01 kJ of energy and 0.25€ of goods to produce one car (Figure 2.2).

The inputs of energy production and of goods production are listed in Table 2-1 and showed in Figure 2.3.

Table 2-1 Inputs related to a unit of output for energy and goods production

	1 kJ of Energy Output	1 € of Goods Output
Energy Input (kJ)	0.0881	0.4
Cars Input (car)	0.5	0.1
Goods Input (€)	0.2	0

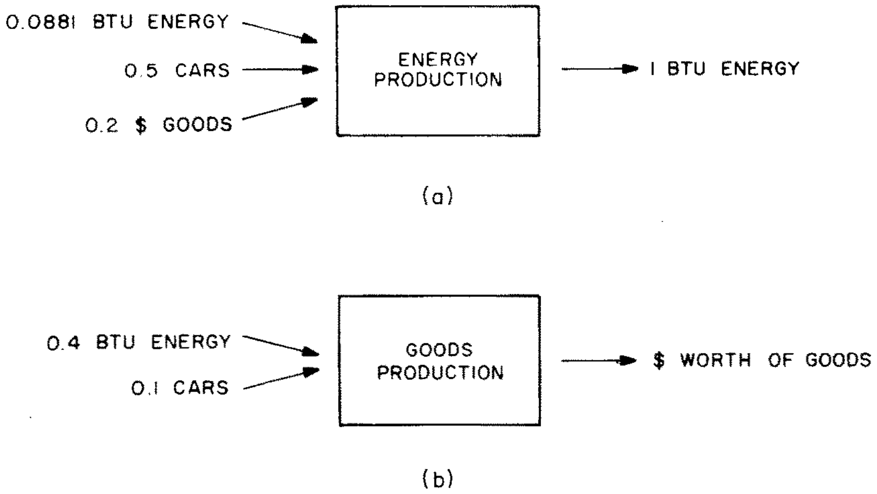


Figure 2.3 Production of energy (a) and goods (b) [55]

At this moment it can be drawn a ‘production tree’, like the one in Figure 2.1, similar to the one in Figure 2.4, where the dashed lines represent the not considered inputs, called ‘truncation points’ [55]. It can be deduced the values of the inputs of the stages that go upstream are scaled according to their output value.

The resulting total energy embodied is 0.152 kJ/car, with an unknown truncation error.

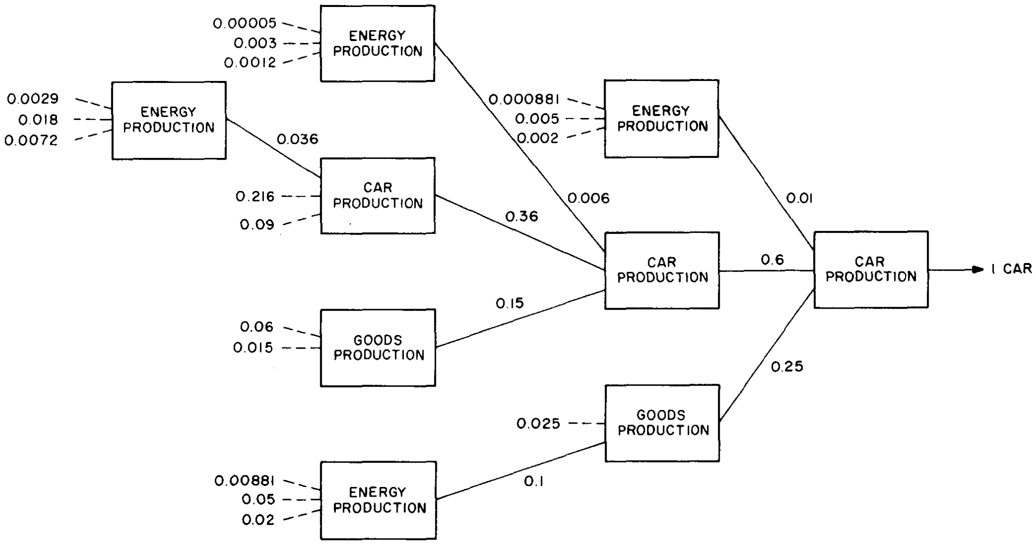


Figure 2.4 Hypothetical 3-sector process analysis [55]

2.1.3 Advantages

The method of process analysis has two main positive aspects, which makes it relevant for its applications:

1. Theoretically allows to trace back all the ‘typical’ inputs, excluding the ones so small that the aggregation error is acceptable [55];
2. If detailed data are available, gives very accurate results [54][56].

2.1.4 Shortcomings

Even for a carefully defined production process there are some inconsistencies that can be attributed to one or more of the following factors [57]:

1. non-comparable units of measurements;
2. uncertainties in the assumptions;
3. measurement uncertainties;
4. data violating laws of physics; and
5. confidential and non-verifiable data and data from unreliable sources.

For each product the amount of data required for its own process analysis can be enormous, due to the complexity of the links between the steps of the process and to numerous branches, mainly secondary supply processes, that can appear going upstream in the same process. Furthermore if one considers that the entire process has to be analysed over the period that goes from its construction till dismantling, well, the amount of data increases. In the end, lack of industries' transparency leaves to limited datasets, nevertheless analyses can still be performed, since usually a product doesn't see in its process more then ten inputs. [58]

Finally, the wide range of products manufactured in developed and developing economies exacerbates the last problem. [52]

Problems in tracing all the upstream processes, make the process analysis framework incomplete [52]. Moreover, "not all processes are amenable to easy modelling and detailed physical description" [59]. Referring to the example of the car (showed in Figure 2.4), in Figure 2.5 is showed that excluding some inputs or interrupting the assessment at the third stage may lead to certain incompleteness and errors (Table 2-2).

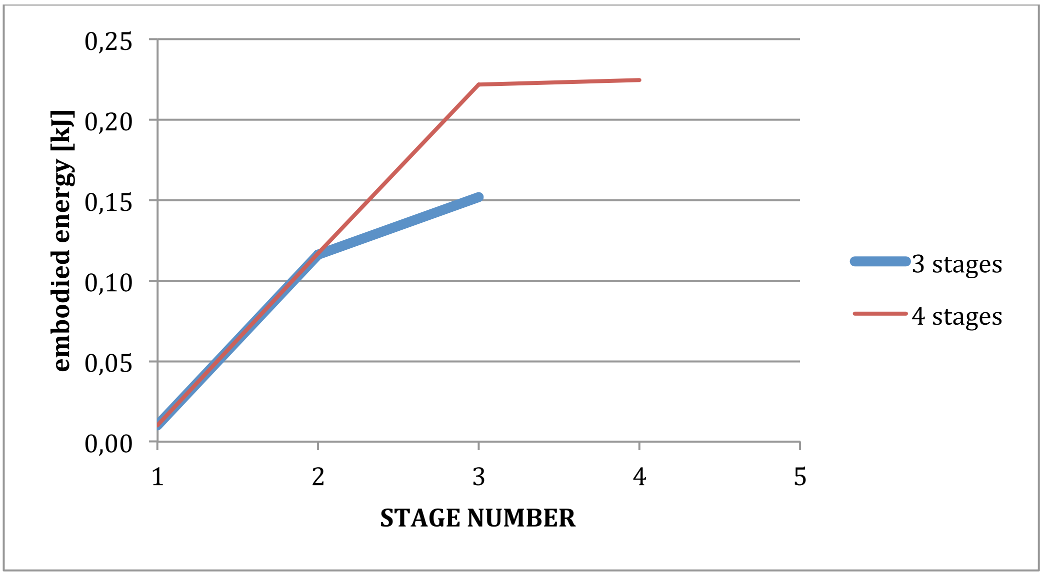


Figure 2.5 In this graph two things are important: first augmenting the number of stages considered the energy embodied in 1 car increases significantly; second in the 3rd stage some inputs were neglected by Bullard, while, if considered, the increase happens first, giving some justifications to the 3rd stage truncation.

Table 2-2 Referring to the process analysis of 1 car production, embodied energy changes in case of inclusion of the previously neglected inputs (46% increase), in the 4-stages assessment the truncation error is small (1.4%)

Embodied energy at 3rd stage		**3rd stage error**	Embodied energy at 4th stage	**4th stage truncation error**
3-stages assessment	4-stages assessment		4-stages assessment	
0.152 kJ	0.222 kJ	**46%**	0.225 kJ	**1.4%**

2.1.5 Applications

Process analysis is more appropriate to specific processes, or manufacturing chains, for which physical flows of goods and services are easy to trace [55]. This kind of analysis is exploited by industrial process engineers, mostly in the chemical process industry such as petrochemicals, aluminum, iron and steel [59].

2.2 Alternatives to process analysis

Process analysis has to be:

- based on detailed modelling of production, distribution, use, and disposal for a specific product;
- able to represent specific technologies and conditions along the life cycle and evaluate variations in these conditions.

But it needs:

- high-input data requirements;
- to cut off some part of the supply chain in order to limit the complexity of the model, so leading to sometimes-significant errors.

Process analyses result being often incomplete because they exclude a large number of small inputs [52]. And since in the industrial sector data requirements are immense and processes data within various firms are not easy to obtain, economic statistics found in input-output tables have been suggested as an alternative procedure, albeit less accurate. [59]

2.2.1 Input-Output Analysis

When it comes to large scale systems the applicability of Input-Output (I-O) analysis remains and its results are pretty exhaustive [56].

I-O analysis is a common technique in the economic field, introduced by Leontief in 1941 [55]. Bullard [4] adapted Leontief's I-O theory using physical quantities for the terms of the linear equations, and not their monetary values.

The I-O model is made of linear relationships between the sectors of an economy or the subsystems of a generic system. Each sector or subsystem has a unique product and "it is characterized by a node in the network equations". [55]

Some relevant limitations of I-O analysis are [55]:

- Technology changes (since base year);
- Uncertainty in base year data;
- Errors due to secondary products and linearity assumptions.

Detailed data sets for I-O analysis are not always available, and so only average results can be obtained. To perform I-O analysis the sectors of the system, due to the data requirements, need to have a certain level of aggregation, but, in a certain way, accuracy is inversely proportional to the level of aggregation. [55]

Of course the necessity of macro-aggregated data requires physical time, that makes this analysis quite slow in obtaining up-to-date results [56].

2.2.2 Hybrid analysis

In theory both process analysis and input-output analysis can lead to the same results. But with hybrid analysis, the errors due to truncation in a process analysis, using results from I-O analysis can be reduced, at the expenses of adding an aggregation error. The latter depends on the aggregation level of the I-O model. [55]

"The results of input-output analysis may be used to estimate the energy embodied in flows crossing the system boundary at any level, by associating each good or service with one of the 368 sectors of the I-O model." [55]

The big advantage of the hybrid analysis is that, if combining properly the process analysis stages with the I-O model, the truncation error from process analysis and the aggregation error from I-O analysis are minimized. [55]

2.3 Typically used process analyses

2.3.1 Material flow analysis (MFA)

2.3.1.1 Definition

Material flow analysis (MFA) is defined as "a systematic assessment of the flows and stocks of materials within a system defined in space and time". The sources, the intermediate and final sinks of a material are connected, and, thanks to the 'conservation of matter' principle, all inputs, outputs and sinks of a process can be controlled by a material balance. [60]

Total material requirement (TMR), which is the sum of the mass of all resources excluding air, water and agricultural tillage [35], is a useful aggregate indicator employed in MFA. Another indicator is the material intensity per service unit (MIPS), defined as the cumulative material consumption per unit of product or service [35].

2.3.1.2 Methodology description

The procedure to perform MFA, as described in Figure 2.6, is mainly iterative and sees first, the boundaries definition together with the selection of the substances and processes to analyse. After that all the balances of goods and substances are performed.

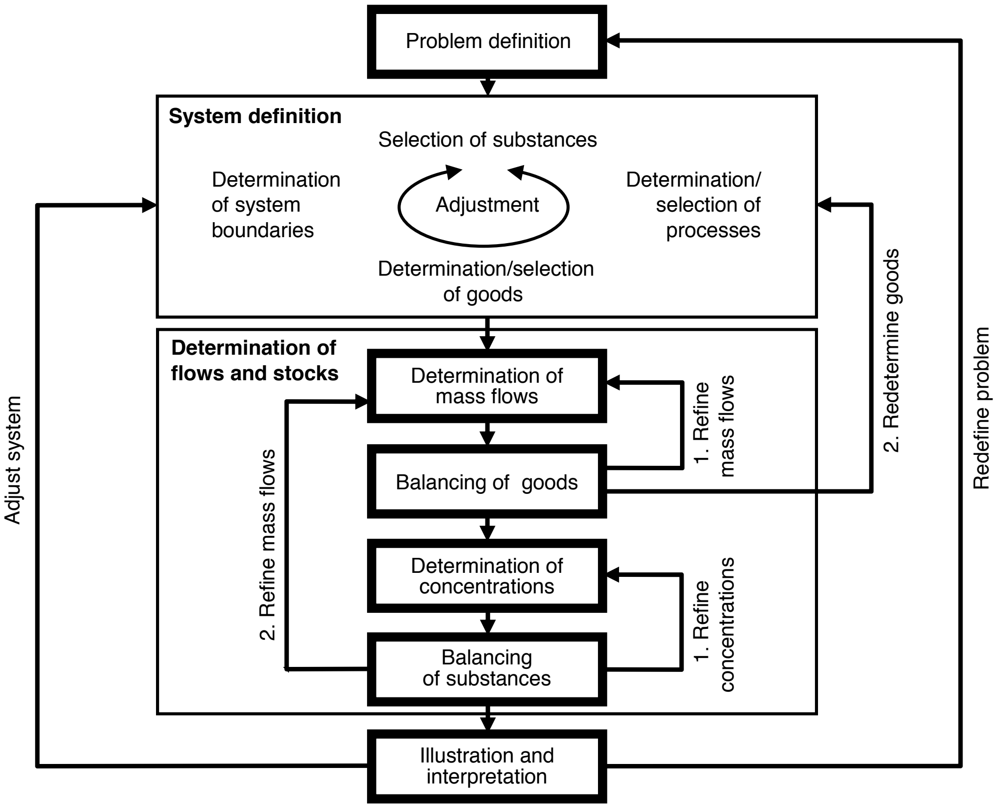


Figure 2.6 Procedures form MFA. MFA is an iterative process. Selections of elements and accuracy of data have to be checked with regard to the objectives of the investigation [60]

The considered categories are six:

1. Biotic materials
2. Abiotic materials
3. Earth movements
4. Water

5. Air
6. Fuels and electricity

A relevant characteristic, in MIPS calculation, is that different materials are not distinguished. So, the same importance is given to 1 kg of coal and 1 kg of copper. Furthermore, to avoid double counting in the MFA, only input flows are accounted in MIPS, because inputs equal outputs. But in the industrial sector inputs are less than outputs. [60]

2.3.1.3 Applications

MFA accounts in physical units encompassing all the life steps of materials (extraction, production, transformation, consumption, recycling and disposals) [61]. For this reason it could be used with the scope of resource conservation and environmental protection [60].

Unfortunately MFA cannot represent resources like land or sunlight, and issues can arise when considering quality differences of materials, because equal mass does not imply substitutability [35]. Imagine adding up 1 ton of copper to 1 ton of oil, since they have different scope in our society, it would be completely incoherent for measuring resource use or consumption.

By the way, MFA is a tool generally used to analyse and characterize material stocks and flows at any boundaries level, global, national or regional [62]. Applications of this method can be found also in fields like environmental management, natural resource management and waste management [60].

2.3.2 Energy analysis (EA)

Energy analysis (EA) in general tries to calculate the amount of energy that is necessary to provide goods and services [56]. Two kinds of analyses are implicitly included when EA is performed: ‘Net Energy Analysis’ and ‘Embodied Energy Analysis’.

2.3.2.1 Definition

‘Energy analysis’ is called “the process of determining the energy required directly and indirectly to allow a system to produce specified good or service” [19].

Bullard [4] defines ‘net energy’ as “*the output of an energy production system determined by taking full account of the energy required for inputs to the process*”. The word ‘net’ means that the balance is calculated over the whole life of the product and all the energy and materials employed in the phases of life (fabrication, maintenance, decommissioning) are subtracted from the overall energy generation [63].

Bakshi et al. [35] define 'net energy' as the difference between the energy content of the product and the cumulative processing energy demand to convert the feedstock into a product, considering only fossil fuels, in formula:

$$E_{net} = \text{energy content of product} - \text{cumulative processing energy} \qquad (2.1)$$

The demand of energy consists of two types: direct and indirect. 'Direct energy' is the one consumed in form of electricity, or fossil fuels; 'indirect energy' is the energy consumed to produce goods and services that will be used by consumers in general [55].

"*Net energy analysis of an energy supply system involves identification and computation or measurement of the energy flows in a society that are needed to deliver energy in a particular form to a given point of use. These flows are then compared to the energy converted or conserved by the particular system under consideration.*"[59]

Net energy analysis obtains as result the 'cumulative energy consumption' (CEnC), which corresponds to the direct and indirect energy consumed for making a product [35]. In general the indirect energy component of the whole consumption is often higher than the direct component [55].

The 'embodied energy' of a product or a service is the energy dissipated to obtain such product or service [56]. Treloar [52] defines 'embodied energy' as "the energy required directly and indirectly in all activities associated with the provision of a good or service, including the amounts consumed in all upstream processes, including fuels manufacture, and the share of energy used in making equipment and in other ancillary functions". While embodied energy analysis is "the systematic study of the inputs and outputs of any process, and the numerical assignment of energy values to each input" [64]. In case of a manufacturing process, the total embodied energy includes the direct energy of the main process and the indirect energy embodied in the material inputs to the process, similar to Figure 2.7. [52]

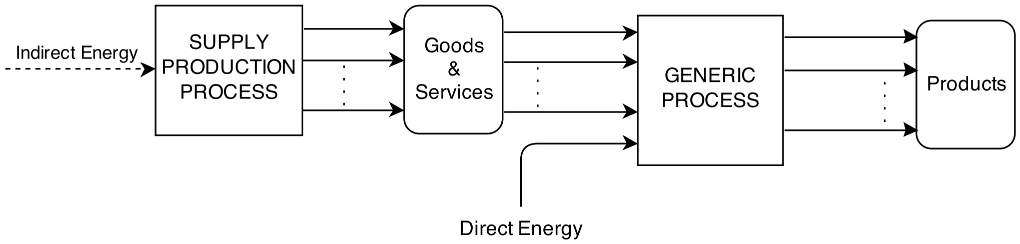


Figure 2.7 Representation of how direct and indirect energy are considered in the production of a generic product

To go thorough this kind of analysis it is also important to define the ‘energy intensity’, which is the embodied energy per unit of product or service for a system, and it is expressed in J/unit (or kJ/unit, MJ/unit) [56]. In some cases, the term ‘energy intensity’ is expressed in kJ/$, like showed in [65], but, basically, is the same, except the fact that instead of the generic unit it is used the sales revenue of that product or service.

2.3.2.2 Methodology description

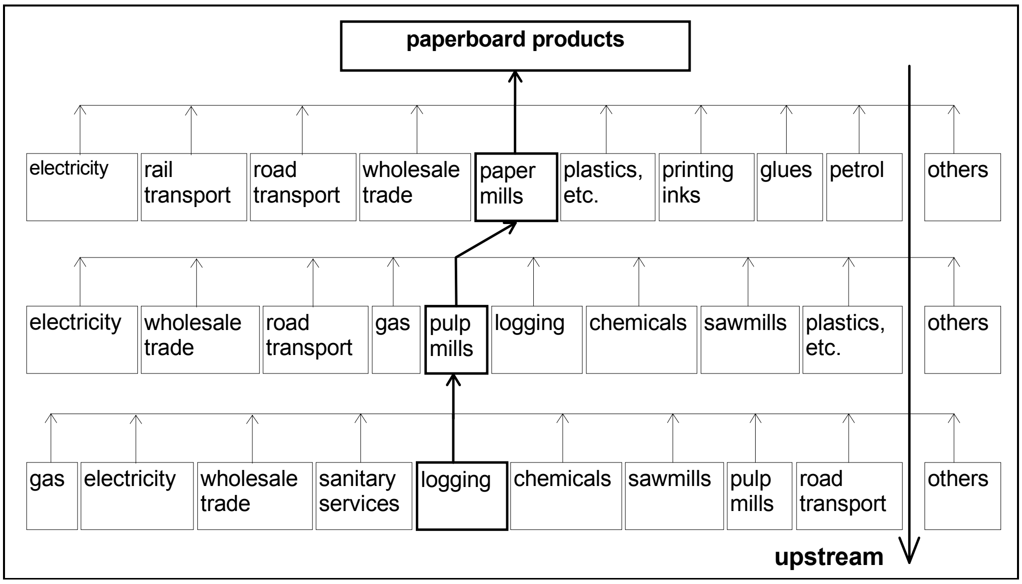


Figure 2.8 Direct and indirect suppliers to paperboard product manufacturers [52]

To assess the energy embodied in a product, the process analysis covers the manufacturer, its suppliers, their suppliers, and so on (see Figure 2.8). At each stage it has to be accounted for all the energy inputs per unit of output, and inputs of everything else. [25]

In Figure 2.9, there is a representation of a generic system *j*, sketched as a box, where material inputs X_{ij} enter into the box multiplied per their embodied energy ε_i (kJ/unit of product), and the energy E_j enters directly in the system [56]. The output corresponds to the amount of product X_j multiplied per its energy intensity ε_j.

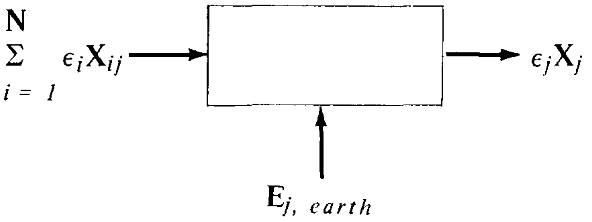


Figure 2.9 Generic system to apply the energy balance [56]

For the system *j*, the 'energy balance' (2.2) can be written to calculate the energy intensity per unit of output[56].

$$\sum_{i}^{N} \varepsilon_i X_{ij} + E_j = \varepsilon_j X_j \tag{2.2}$$

On the left hand side of the balance (2.2) there is the CEnC relative to the output of system j. If the output X_j were a unit, then the CEnC would correspond to the energy intensity of the output ε_j.

In 1974, the IFIAS created a framework classification model (Figure 2.10) for the purpose of comparing different studies. [52][19]

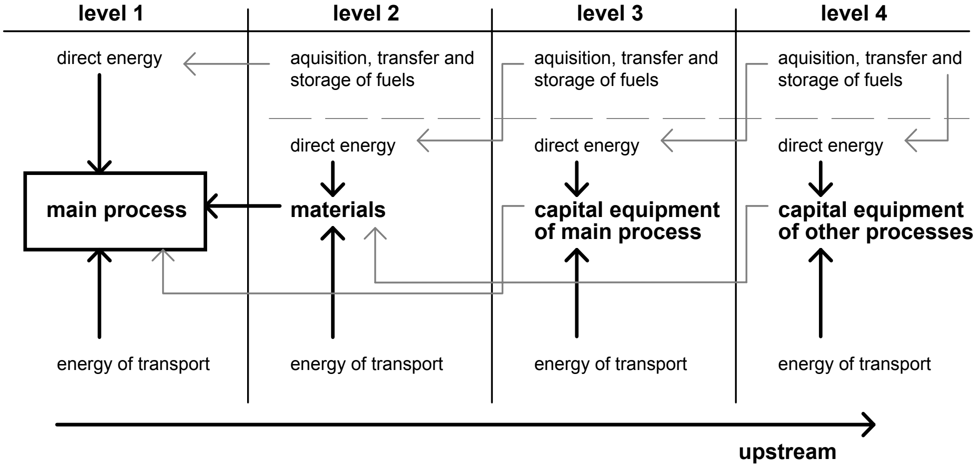


Figure 2.10 IFIAS classification model for embodied energy analysis frameworks [52]

The scheme proposed by IFIAS divides an energy-and-technological network in four levels [66], as in figure:

- Level 1: immediate consumption of semi-finished products and energy carriers in the final stage of the production, including the consumption of energy for transportation;

- Level 2: immediate consumption, with the transportation, of semi-finished products and energy carriers to fabricate the semi-finished products and energy carriers of the first level;
- Level 3: fabrication of machines and installation of the first level;
- Level 4: fabrication of machines and installations for the production of machines and installations operating in the first level, together with the production of semi-finished products and energy carriers for the third level.

2.3.2.3 Applications

The concern about the dependence of the United States on limited and non-renewable energy resources, mainly motivated the scientists in the 1970s [4]. Wright, among the firsts, calculated energy requirements to produce goods and services [67]. For Chapman [68] energy analysis would be very useful in the estimation of natural resources.

This approach has the ability to quantify the consumption of fossil fuels, but neglects the role of nonfuel materials [35]. It fails also when evaluating similar energy streams that result on possessing different available energy.

One reason to perform an energy analysis is seeking for energy conservation and for potential energy saving when substituting products or services [56]. Another application could be investigating the feasibility of a proposed energy production technology [4].

Three features of process analysis can be highlighted in the energy flow context [59]:

1. having or estimating all the data of a process, its maximum energy efficiency can be calculated using the laws of thermodynamics;
2. no importance is given to impacts of the plant functioning on upstream or downstream processes;
3. to assess all the energy flows interconnected with the analysed system, one should have a dataset that includes specific information on energy flows at an industry-wide level.

2.3.2.4 A practical example: Ethanol vs. Gasoline

Table 2-3 Comparing energy inputs to produce fuel for internal combustion engines (adapted from Schulz [69]**)**

	Energy inputs (in MJ) to generate 1 MJ from fuel		
	Petroleum	*Natural Gas*	*Coal*
Ethanol	0.04	0.28	0.41
Gasoline	1.10	0.03	0.05

Here it is reported the comparison, made by Schulz [69], between ethanol and gasoline's net energy, of which data are showed in Table 2-3.
Ethanol's net energy is:

$$E_{net,ethanol} = 1.0 - \underbrace{(0.04 + 0.28 + 0.41)}_{\text{CEnC}_{ethanol}} = 0.27 \text{ MJ} \tag{2.3}$$

While for gasoline results:

$$E_{net,gasoline} = 1.0 - \underbrace{(1.10 + 0.03 + 0.05)}_{\text{CEnC}_{gasoline}} = -\ 0.18 \text{ MJ} \tag{2.4}$$

So,

$$E_{net,gasoline} < E_{net,ethanol} \tag{2.5}$$

which means that ethanol should be preferred over gasoline.
As pointed out by Schulz [69], this result does not consider potential environmental degradation or available land, which are relevant factors for food production.

2.3.3 Entropy Generation Minimization (EGM)

2.3.3.1 Definition

Likely when mass or energy analyses are performed, *entropy generation analyses* can be fulfilled considering the irreversibilities that appear during the functioning of the system under consideration [70].
The method called 'entropy generation minimization' (EGM), also known as 'finite time thermodynamics', has as objectives the modelling and the optimization of real components to assess their irreversibilities due to heat transfer, mass transfer and fluid flow [34]. The optimization of the model allows to better perceiving the concept of entropy generation showing, for example, "how it impacts thermodynamic performance" [34].
The critical aspect of the EGM method is the minimization of the entropy generation rate [34]. To perform irreversibility minimization "of a proposed design the analyst must use the relations between temperature differences and heat transfer rates, and between pressure differences and mass flow rates [34].

2.3.3.2 Methodology description

Through the so called 'ecological function' (2.6) [71] (almost identical to the Gouy-Stodola theorem), the 'thermal efficiency' η_E can be maximized.

$$\dot{E} = \dot{W} - T_0 \dot{S}_{irr} \tag{2.6}$$

$$\eta_E = \frac{\eta_C + \eta_{CA}}{2} \tag{2.7}$$

In (2.6),

- $\dot{W}$ is the power of a plant operating between two reservoirs at temperatures T_1 and T_2, look Figure 2.11;
- T_0 is the environment temperature (which may correspond to T_2 of Figure 2.11); and
- $\dot{S}_{irr}$ is the rate of entropy generation.

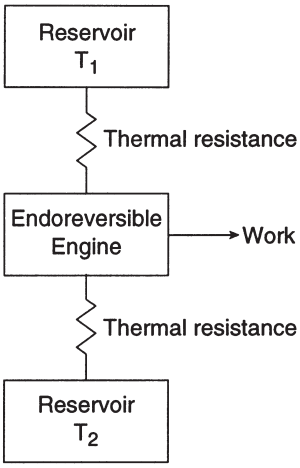


Figure 2.11 Schematic view of an endoreversible engine [71]

Moreover in (2.7) the terms η_C and η_{CA} are respectively the Carnot efficiency and the Curzon and Ahlborn efficiency [71], which corresponds to the maximum power regime [72].

$$\eta_C = 1 - \frac{T_2}{T_1} \tag{2.8}$$

$$\eta_{CA} = 1 - \sqrt{\frac{T_2}{T_1}} \tag{2.9}$$

2.3.3.3 Applications

EGM can be used for different scopes [34]:

- Minimization of entropy generation in heat exchangers,
- Maximization of power output in power plants,
- Maximization of an ecological benefit [72], and
- Minimization of cost.

It has been showed [72] the maximization of η_E is a good optimization criterion, which is also compatible with ecological objectives.

2.3.4 Exergy-based analysis

"The exergy analysis is the modern thermodynamic method used as an advanced tool for engineering process evaluation" [73].

Exergy-based methods can satisfy both first and second thermodynamics laws including together material ad energy streams [74].

Exergy analysis is useful to improve process efficiency, because limiting exergy losses equals to limiting the resources for the functioning of systems [50]. With this methodology thermodynamic imperfections are quantified as 'exergy destruction' [26].

Applications in the industrial sector can be: thermo-mechanical and manufacturing processes, chemical and synthesis processes [49].

Some of exergy analyses try to examine economic sectors but still it is not jet a diffuse practice [74]. In the last two decades, some example of societies analyses, using exergy, have been developed: China [75]–[80], Siena (Italy) [81], United States [82], Japan [83], household buildings [84], [85], Turkey [86], [87], population dynamics [88], [89], Norway [90], Nova Scotia (Canada) [91].

"Exergy analysis may constitute a useful tool for identifying strategies for improving energy efficiency, as improved system alternatives. If such a strategy has then indeed been effective in reducing various forms of energy resource use (e.g. oil, coal, uranium) is a matter of LCA inventory modelling of the alternatives concerned, comparing these, and other, environmental interventions."[92]

Rosen [93] affirmed that ecosystem exergy analysis can measure the disorder increase in ecosystem associated with the human environmental impact.

2.3.5 Comparison of process analyses

Table 2-4 Comparison of process analysis methodologies among different numeraires

Numeraire (Method)	Pros	Cons
Mass (MFA)	It is basic to perform the other methods;	Ignores the inputs of ecological services [50]; Does not consider other properties of a material except its mass [74];
Energy (EA)	(Energy balances) is the basis for exergy balance[73]; "Establishes the priority of the process requiring consideration" [73]; Able to value all types of material and energy flows without violating physical laws [50]; Implicitly tries to minimize fossil energy inputs per unit of output [25]; Energy analysis can consider labor, as a fraction of the total fuel energy used in support of human service [25];	Does not take into account the process direction [73]; Does not incorporates different qualities of energy [73][94]; Do not consider potential environmental degradation or available land [69]; Provides misleading indicator, aggregating diverse resources using the same metrics [35][69]; "Do not quantify the environment's role in absorbing and processing pollution [25]; "Do not recognize the qualities of energy across the energy spectrum of the biosphere", ignoring "half of the total energy driving the economies of the biosphere"[25]; "Embodied energy in goods and services does not include the environmental support derived from solar, geophysical and tidal energies that drive all economies" [25];
Entropy (EGM)	Shows thermodynamic inefficiencies of processes [15]; Traces hypothetical starting points for optimization [15]; Combines matter and energy, with both quantitative and qualitative focuses [15]; Measure the loss of potential utility (e.g. potential energy) [15]; Not arbitrary *reference state* [15];	"Entropy content cannot be used for evaluating the absolute utility of a resource, it only accounts for utility changes" [15]; Entropy cannot consider potential energy changes [15]; "Entropy is complex and abstract indicator"[5];
Exergy (Exergy-based analysis)	Is able to account for fuel and nonfuel resources such as materials [35]; Account for the first and second laws of thermodynamics [35]; Material resources result in a more meaningful metrics for decision making [95]; Units comparable with energy [5];	Provides misleading indicator, aggregating diverse resources using the same metrics [35]; A reference environment must be defined [15]; Exergy of substances depends on the context of their use and the available processes [15]; Not clear when common baselines (R.E.) are used [5]; Ignores capital and labor [96];

3 Thermo-economic process analysis for natural resource consumption

Thermoeconomics exists as a general theory of useful energy saving, where cost formation process is the link between physics and economics.

Thermoeconomic analysis encompasses thermodynamics and economics applying the concept of cost to exergy. Representing the irreversibilities of a process with exergy destruction allows using it for costs allocation, and that seems adequate when true inefficiencies of industrial processes have to be reduced. Exergy is always destroyed in common processes, since they are not reversible, but also some natural resources are consumed and lost forever, which involves a cost in economic terms. It comes naturally that, the more a process is irreversible the more natural resources are consumed [97].

When exergy balances are carried out,

$$Ex_{Input} - Ex_{Output} = Irreversibilities > 0 \tag{3.1}$$

only irreversibilities of processes come out, while everything else is categorized either as an input or as an output. After defining the product of a process its efficiency can be computed as:

$$Efficiency = Product / Resources \tag{3.2}$$

To understand if a process has a good efficiency residual products have to be showed into the exergy balance,

$$Resources(F) - Products(P) = Residues(R) + Irreversibilities(I) > 0 \tag{3.3}$$

In this way the ‘purpose’ of a process can guide the analyst when performing the analysis, keeping in mind that the flows crossing the boundaries of a system can be:

- The production objective;
- The resources required to carry out the production; and
- The residuals.

These categories are not defined by the Second Law but are very important in the connection of physics with economics [97]. The outputs of a system can be various but the wanted products may be less then the outputs, and

they should be defined a priori. Only after that, efficiencies' gains and reduction of resources consumption can be pursued, or comparison between systems with the same products can be made.
Looking at the efficiency definition (3.2), its inverse results to be:

$$Unit\ Consumption = Resources/Product \tag{3.4}$$

Which can be regarded also as the 'average cost of a unit of product'.
Torres and Valero, in [97], propose chain of concepts that allows connecting physics with economics, see Figure 3.1.

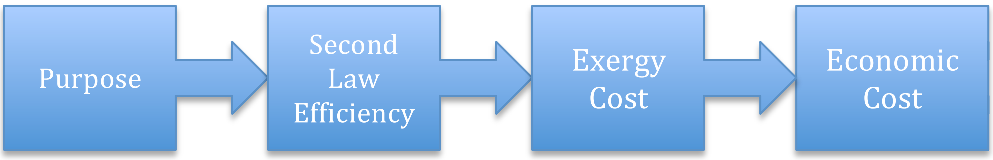


Figure 3.1 Logical Chain of thermoeconomic concepts (adapted from [97]**)**

With thermoeconomics, cost of consumed resources, system irreversibilities and money can be assessed, and this helps showing how reduction of resource usage can be obtained.
Some of the applications of thermoeconomic analyses are:

- rational prices assessment of plant products based on physical criteria;
- optimization of specific process unit variables to minimize the final product cost, i.e. global and local optimization;
- detection of inefficiencies and calculation of their economic effects in operating plants, i.e. plant operation thermoeconomic diagnosis; and
- evaluation of various designs alternatives or operation decisions and profitability maximization.

3.1 Exergy Cost Theory

In previous chapters it has been showed that exergy-based analyses associate useful energy to flows in a process or to a thermodynamic system. Thinking that a user pays only the useful part of an energy carrier, then, exergy is strictly related with the cost, not with the price, of the energy carrier, a part of the fact that exergy can measure objectively the thermodynamic content of the same factor. [97]
After the first global energy crisis in the 1970s, the concept of embodied energy started to appear but it lacked of good allocation techniques when there was more than one product simultaneously produced [97]. Both

Valero and Szargut proposed to use exergy instead of energy, with their respectively exergy cost [98] and cumulative exergy consumption [37].

Cost corresponds to the amount of resources, in general, used to create a product. So, the purpose of production is linked with the concept of cost. It is important to notice that the cost is a property of the product but cannot be found in the product itself, because it depends on the structure of the system or process. Cost will appear only after the system analysis, and in case of a mass or an energy stream, its cost is the amount of energy necessary to produce them.

Exergy cost, B^*, definition [99]: for a given a system, after defining its limits, its disaggregation level, and production aim of the subsystems, for a physical flow the exergy cost represents the amount of exergy that is necessary to produce this flow. It follows that exergy cost is, like exergy (B), a thermodynamic function.

Valero and Torres [97] describe:

- Unit exergy cost,
- Monetary cost,
- Unit monetary cost.

The *unit exergy cost* of a stream is the amount of exergy required to get a unit of the product stream. The *monetary cost* represents the amount of money to generate a mass or an energy flow, and can consider the economic cost of the used fuel c_F (€/MJ) or the cost of installation and operation of a plant Z (€/s). The *unit monetary cost* is the amount of monetary units per unit of exergy required to obtain the indicated flow [97].

The *exergy costing principle* states that “exergy is the only rational basis for assigning monetary values to the interactions an energy system experiences with its surroundings and to the thermodynamic inefficiencies within the system” [97].

For a product, two types of costs can be identified:

- ‘direct costs’, which are linked the resources used exclusively to the realization of the product; and
- ‘indirect costs’, basically all the non-direct costs.

The cost of a flow is strictly associated to the production process, and it is not a separate thermodynamic property of the flow. Moreover, other costs, interconnected with the first one, have to be determined. Some of these costs can be classified as external or internal, depending on the system limits.

Two main reasons why the exergy cost is extremely important in thermoeconomics are:

- the physical concept of irreversibility is related with the economic concept of cost; and
- assessing mathematically the relationship between local irreversibilities and the global impact on natural resources using the exergy cost allows understanding and giving a meaningful basis to thermoeconomic diagnosis.

3.1.1 Exergy Cost accounting

In businesses, cost data are used to make decisions, and evaluating and controlling performances. The main objective both for individuals and companies is cost optimization or even minimization, because cost signifies loss of resources and when scarce resources come into play cost minimization is the only goal. Hence cost accounting represents a technique for estimating how cost of services or products will differ among alternatives [97].

Cost accounting seeks to:

- define the actual cost of products;
- provide a rational basis for evaluating products;
- procure means for monitoring costs; and
- shape a basis to evaluate and operate decisions [97].

Assessing each cost of the internal flows of a system, if compared with standard cost values, unnecessary resources consumption could be avoided, so as to accomplish the purpose of thermoeconomic diagnosis.

Considering any energy system, the exergy of resources is always greater or at least equal to the exergy of products, like in (3.3), in symbols:

$$F - P = I \geq 0 \tag{3.5}$$

Therefore, the exergy of the resources consumed corresponds to the amount of exergy needed to obtain the products.

Taking a generic production chain, in each step some exergy can be added or destroyed. Starting from the deposits, if one follows all the production line, accounting for all the wastes, feedbacks and recycles, up to the final product, will obtain the exergy cost of the commodity, which corresponds to the cumulative exergy 'embodied' in it. This technique can be applied to any good or service consumed within a society.[49]

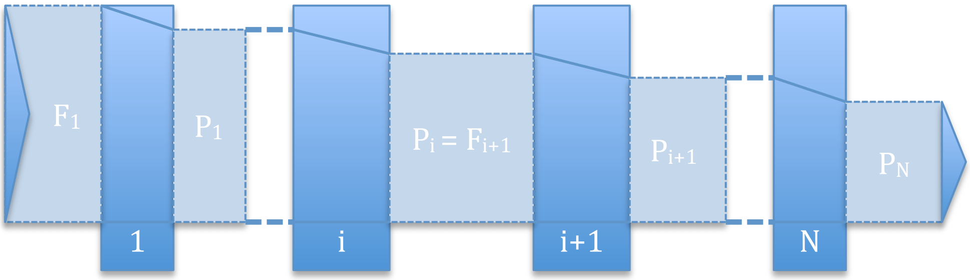


Figure 3.2 Process of N steps with purpose of producing only product P_N (adapted from [97]**)**

Imagine a process with N steps and every step has only one product, like in Figure 3.2. In each *i*-th step there is an amount of resources F_i entering and an amount of semi-finished product P_i exiting; moreover resources entering in the step *i+1*, F_{i+1}, are equal to the product P_i coming out the step *i*. Since in each step part of the resources are sacrificed it is true that:

$$F_i \geq P_i \tag{3.6}$$

And looking at the overall process

$$F_1 \geq P_N \tag{3.7}$$

Where F_1 is the total amount of resources required to obtain the desired product P_N, and it can be also defined as the cost of the product P_N.

3.1.2 Cost balance

A general formulation of the cost balance for the entire system or just for a generic component can be written as:

$$\sum_{i \in IN} c_i \dot{B}_i + \dot{Z} = \sum_{j \in OUT} c_j \dot{B}_j \tag{3.8}$$

where

- $\dot{B}_i$ is the exergy of the input flows of the system or component;
- $\dot{B}_j$ is the exergy of the output flows;
- c_i represents the unit cost of the *i*-th input flow;
- c_j is unknown and has to be determined for the *j*-th output flows; and
- $\dot{Z}$ is the cost of installation and operation of the plant.

For a single product it is simple and easy to determine the unit cost of the output. But for a multi-product system, criteria have to be added to the balance (3.8), and exergy can be employed in supporting the cost allocation of products. One theory is explained in appendix.

3.1.3 Issues with aggregation

Thermodynamic methods have the advantage to allow *aggregation* of a variety of resources in a scientific exact manner [35]. With this tool, life-cycle aspects of substitute products can be easily compared [35]. If resources are combined, aggregate metrics help in their substitutability aspect, but always paying attention on not losing information [35].

4 Exergy-based methods for thermoeconomic process analysis: a review

In the following section it will be given a description of the exergy cost accounting methods that are mostly used in the scientific community and the ones that have been repeatedly found during the bibliographic research phase.

Each paradigm will be described with the following framework:

- Description
- Impact categories
- Applications
- Additional notes.

A pros and cons comparison will be showed at the end of this section.

For all the analysed paradigms it has been hard to find correspondence between the calculation framework, the terminology and the impact categories used. It is hoped that this chapter could bring some help in the understanding and comparison of these methodologies.

All methodologies are characterized by a life cycle approach, which includes in the analyses all the phases of life of the product or system under consideration, including its production or construction, its operation and its disposal [92].

Some other methods were identified (ECEC and ECExC), but due to the insufficient bibliographic materials no attention will be given in this work.

4.1 Cumulative Exergy Consumption (CExC)

4.1.1 Definition

The *Cumulative Exergy Consumption* (CExC) expresses the sum of the exergy content of natural resources consumed in all the steps of a production process [66]. Someone uses the terminology Cumulative Exergy Demand (CExD) but it is equivalent to CExC [100], and they are both expressed in kJ/unit of product.

The CExC is important because in a production process the last stage can be very exergy efficient while the previous ones couldn't. This approach lets the analyst the possibility to find out all the exergy losses generated in all the steps of the production process of a final product, reaching till to the stage where natural resources are extracted from the environment. [37]

4.1.2 Impact categories

The categories of impact considered in CExC are all the kinds of natural resources, even the renewable ones [66].

The CExC takes into account not only the energetic resources, but also the exergy content of non-energetic raw materials withdrawn from the environment [37].

A list of the resources taken into consideration by this methodology follows here below [100]:

- Minerals (minerals, rocks, non metallic ores)
- Metal ores (metallic ores)
- Water (all types of water, excluding water of hydroelectric power plants)
- Biomass (all types of biomass)
- Hydro-energy (potential energy in barrages)
- Wind, solar, geothermal energy (energy from wind, radiation and geothermy)
- Nuclear energy (energy from fission of uranium)
- Fossil energy (crude oil, natural gas and peat)

4.1.3 Application

Some applications proposed by Szargut et al. [37] are listed here below:

- calculation of the necessary increase of raw materials and fuels extraction for a planned increase of production of the product under consideration;
- evaluation of the influence of price changes of raw materials and of fuels on the production costs of the product under consideration;
- comparison of the cumulative consumption of raw materials and fuels resulting from different production methods of the same product;
- determination of a possible decrease of the consumption of raw materials and fuels as a result of the introduction of a new production methods;
- analysis of the cumulative effects which can be achieved by the utilization of waste products;
- analysis of the cumulative effects which may result from the substitution of raw materials and fuels in the event of scarcity of one or the other.

Szargut used CExC to assess the non-renewable exergy burdening the products of cogeneration processes [101]. In [37] all the typical industrial processes are analysed. Some of the processes that have been analysed with the CExC paradigm are, for example:

- Production of calcium carbide [66];
- Cogeneration of heat in steam HP-plant [66];
- Blast furnace for pig iron production [101].

4.1.4 Additional Notes

For Bakshi et al. [35] CExC analysis is "similar to energy analysis, but uses exergy instead of energy".

Bösch et al. [102] used the notation CExD (Cumulative Exergy Demand) in order to compare CExC with Cumulative Energy Demand (CED), but the method used doesn't change.

Efficiency in CExC's field is called 'cumulative degree of perfection' (CDP) [37], [103], viz:

$$CDP_i = \frac{b_i}{r_i} \tag{4.1}$$

where CDP_i is related to a generic product *i*, b_i is the specific exergy of the product and the r_i is called CExC index obtained with (4.2).

$$r_i = \frac{B_i}{P_i} \tag{4.2}$$

Where B_i is "the sum exergy of natural resources delivered to the system in all the steps of the chain of production process leading to the product under consideration" [4]; P_i is the "net production if the product *i* in the system under consideration" [4]. Both B_i and P_i are related to the same time interval.

4.2 Thermo Ecological Cost (TEC)

4.2.1 Definition

A measure of the depletion of non-renewable resources is the concept of *thermo ecological cost* (TEC), introduced by Szargut in 1978 [104]. It is an expression of the cumulative exergy consumption of non-renewable resources along the entire production process of a commodity. For this paradigm the word 'thermo' is used because TEC is an exergetic-kind of cost, which means it does not use monetary units [35] [104].

4.2.2 Impact categories

However the natural resources taken into account are the non-renewable ones, the TEC approach distinguishes two kinds of categories:

- ‘Fuel’ resources: non-renewable energy resources
- Mineral resources.

Fuel resources can be replaced using renewable natural exergy resources; mineral resources cannot be supplanted by any other renewable mineral resources, because they do not exist [104].

When the TEC considers only the fuel part the subscript ‘f’ is used, while for the mineral part ‘m’ is the subscript [104].

4.2.3 Application

The TEC approach is employable to determine optimum design and operation parameters or to select the production technology, when the objective function is to minimize depletion of non-renewable resources [35] [104] [105].

Also for the entire globe, or for some region or country the calculation of TEC may be performed. In this case remember that data characterizing export and import of raw materials and products should be taken into account [104].

4.2.4 Additional Notes

Table 4-1 TEC and fuel fraction of some products. Note that 'j' correspond to the typical unit to measure each product

Product	TEC MJ/[j]	z_j
Coking coal	31.20	1.000
Natural gas	835.86	1.000
Electricity	3.42	1.000
Coke	47.44	1.000
Sinter	5.95	0.997
Pig iron	30.46	0.999
Hard coal	27.08	1.000
Oxygen	156.41	1.000
Lime	8.38	0.981
BOF steel	27.40	0.999
EAF steel	12.12	0.999
Metallurgical products	27.16	0.999
Sulphur	24.60	0.223
Copper ore	0.97	0.382
Copper	169.48	0.987
Cement	5.91	0.959
Copper products	304.47	0.993
Machines and devices	193.77	0.999

When calculating TEC values within a region or a country, one should be aware that technology of electricity production ad transportation system could influence them strongly [35]. Moreover, in case one considers the electricity produced from renewable resources, it has to take into account the fuel and the mineral part of TEC of the investments and operational means [104].

The calculation of TEC can be performed by means of a set of balance equations. Each of them contains the TEC of the following delivered components: the used domestic raw materials and semi-finished products, the wear of the machines and installations used in the considered production process, the imported raw materials and semi-finished products, the immediate consumption of nonrenewable exergy extracted from nature, and the compensation cost of losses that are due to the emission of deleterious products. On the side of products of the considered process, there appear to be TECs of the major products and of the useful by-products. The TEC of the useful by-product should be expressed by the value of the TEC of major products fabricated in another process. The substitution ratio between the by-product and the replaced major product should be taken into account. The value of the TEC of imported semi-finished products can be determined by taking into account the fact that the financial means for import are gained by export. Hence the TEC value of the imported semi-finished product results from its monetary cost and from the mean TEC value of the monetary value of exported goods.

The set of balance equations should be formulated and solved only for the semi-finished products used in other production processes. If the considered useful product is not used in other production processes (or used in a very small portion), its TEC may be determined individually by means of a sequence method, which begins in the final step of the production chain and goes back through all the steps until the semi-finished products considered in the mentioned balance equations are obtained. [35]

The balance equations are mutually dependent if some useful product is applied as a raw material in another production process. Only in that case a system of balance equations should be formulated. In the case of ready consumption products the balance equations are mutually independent and can be used by means of a sequence method, beginning with the product and going back through all the production steps. The balance equations may be formulated according to the principles of life cycle assessment, LCA. [106][104]

4.2.4.1 System of balance equations

The total TEC value of products corresponds to the sum of the inlets exergy values.

The calculation of TEC_f and TEC_m is made in two steps:

- Formulation of the general balance equation, like the (4.3) [107]
- Formulation of another balance equation that contains the unknown fractions of the TEC_f in the total value of TEC, and that is independent from the first equation (4.4)[104].

$$\rho_j + \sum_i \left(f_{ij} - a_{ij} \right) \rho_i = \sum_f b_{fj} + \sum_m b_{mj} + \sum_k p_{kj} \zeta_k + \sum_r a_{rj} \rho_r \tag{4.3}$$

Where:

- ρ_j — Specific TEC of the major product of the considered jth process
- ρ_i — Specific TEC of the major product of the ith process delivering the semi-finished products and energy carriers
- f_{ij} — coefficient of production of the ith byproduct per unit of the jth major product;
- a_{ij}, a_{rj} — Coefficient of the consumption of the ith domestic and rth imported semi-finished product per unit of the jth major product;
- b_{fj}, b_{mj} — Exergy of the fuel and of the mineral raw material immediately extracted from nature, per unit of the jth major product;
- p_{kj} — Emission of the kth waste product per unit of the jth product;
- ζ_k — Specific TEC of compensation of the deleterious impact of the kth rejected waste product.

Each balance equation defining the TEC includes in the *outflow side* the specific TEC value of the major product and the values of the connected useful byproducts [104]. In the calculation of TEC, the secondary raw materials obtained after the system dismantling should be included among the outflow components, as the byproducts. On the inflow side of the balance equation there are: the TEC values of the domestic raw materials and semi-finished products, together with the imported ones; the consumption of the non-renewable exergy extracted from nature; the TEC values of the deterioration of machines and installation; and the TEC of compensation of losses due to the dismissal of wastes [104].

The values of ρ_j, ρ_i are unknown in the equation (4.3). The second system of balance equations independent from the first one determines the fuel part of TEC:

$$z_j\rho_j + \sum_i \left(f_{ij} - a_{ij}\right) z_i\rho_i - \sum_r a_{rj} z_r\rho_r = \sum_f b_{fj} + \sum_k p_k z_k \zeta_k \tag{4.4}$$

where:

- z_j , z_i , z_r , z_k — the fraction of fuel part of the considered quantity.

The values of z_j, z_i are unknown in the second equation systems. In (4.3) and (4.4) the components with b_f , b_m appear only when considering the mines extracting raw materials from nature.

The TEC of the imported materials results from the assumption that the financial means for the import are gained by export. Hence the values of TEC of imported materials results from their monetary cost and from the mean TEC-value of the monetary unit of export:

$$\rho_r = \frac{\sum_e S_e\rho_e}{\sum_e S_e D_e} D_r = D_r\rho_m \tag{4.5}$$

where:

- D_r, D_e — monetary cost per unit of the imported and exported product;
- S_e, ρ_e — number of units of the annual export of the eth product and its index of the total TEC;
- ρ_m — mean value of the total TEC per monetary unit of export.

The so determined values of TEC of the imported materials should be divided into the fuel part and mineral part using the proportions appearing in the domestic production:

$$\rho_r z_r = \frac{\sum_e S_e z_e \rho_e}{\sum_e S_e D_e} D_r = D_r\rho_m z_r \tag{4.6}$$

where:

z_e — fraction of the fuel part of TEC of exported products.

The values of z_e, and ρ_e can be determined by means of a difficult iterative method.

4.2.4.2 Byproducts

Every byproduct should be valued as if it were the major product fabricated in another process, so a replacement ratio between the byproduct and the replaced major product has to be used [104].

4.3 Exergetic Life Cycle Assessment (ELCA)

4.3.1 Definition

Exergy accounting can be applied to life cycle assessments–leading to exergetic life cycle assessment (ELCA). The ELCA follows the criterion of life cycle irreversibility, accounting for all the exergy losses occurring during the entire life cycle. Knowing which component causes the losses, the problem of natural resources depletion can better be addressed reducing those losses. Cornelissen and Hirs [108] imply that "when the ELCA is used separately, it is often used to reduce the use of natural resources or the costs associated with their use", while it usually could be used together with LCA to calculate other environmental impacts.

4.3.2 Impact categories

Energy and Materials like in CExC methodology are the used categories.

4.3.3 Application

ELCA can be used in two ways:

1. to determine the consumption of natural resources and
2. to calculate the depletion of natural resources.

In the latter case, a difference has been made between renewable and non-renewable exergy resources to calculate the depletion. [108]

To calculate the depletion of natural resources we have to make a difference between renewable and fossil resources. This situation can be compared with the CO_2 problem. When renewable resources are used the CO_2 emission of using these resources, for example in the case of wood, does not increase the green house effect. In the LCA method according to Eggels [5], the positive effects of this using renewable fuels instead of fossil fuels is assigned, when the CO_2 emission is absorbed by the renewable. In this paradigm the renewable exergy resources is treated in the same way. The positive effects of the exergy absorption are assigned on the moment when the exergy is absorbed in the renewable fuels. For the sake of simplicity the exergy input of the sun and the irreversibility during the transformation of solar exergy into renewable fuels is left out. The exergy input of the sun is seen as "free". In formula form:

$$\dot{D}^{\text{natural resources}} = \dot{I}_{\text{Life cycle}} - \dot{E}^{\text{renewables}} \tag{4.7}$$

where

- D is the depletion,
- I is the irreversibility and

- E is the exergy.

In the models it means that for calculating the depletion the exergy content of the renewables, in this case wood, has to be subtracted of the life cycle irreversibility. However, because no complete life cycle has been analyzed, but only a part of it, negative values for the depletion are calculated. This means that renewable exergy carriers are generated. In a complete life cycle (from cradle to grave) the depletion of natural resources will be positive or zero.

Another way of calculating is leaving out the renewable exergy completely. For every exergy stream has to be found out if it is renewable or not. However, more research is needed to find out which approach is preferable. [108]

4.3.4 Additional Notes

The available exergy values are calculation results based on outdated thermochemical data sources; some go back to the 1950s. It has been proposed proposed an updated set of elements exergies. It should, however, be noted that only geochemical data were updated, not thermochemical data (Gibbs free energies of formation), as they are identical to those implemented previously, apart from sillimanite. New extensive thermochemistry databases have been made available meanwhile. [109]

Chemical exergy is considered to be the most important contribution to the exergetic value of numerous natural resources, because it well reflects their deviation from the reference environment [109]. To compute the chemical exergy of an asset, a reference compound has to be considered for each element inside the asset [109]. This ground state compound is the most probable product of the interaction of elements with other compounds and it is highly stable from a chemical point of view. Knowing the free energies of reaction and having the exergies of the reference species, the chemical exergy of any resource substance can be computed. Sometimes the exergy values result negative; in this case the chosen ground state has to be replaced with a new one.

4.4 Cumulative Exergy Extraction from the Natural Environment (CEENE)

4.4.1 Definition

The exergy method proposed by Dewulf et al. [110] is defined as Cumulative Exergy Extracted from the Natural Environment (CEENE). It aims to quantify the exergy that the natural ecosystem is deprived of over the life cycle of a commodity, and to perform a comprehensive resource-based life cycle impact assessment [111].

4.4.2 Impact Categories

The deprivation of exergy from natural environment that is considered in CEENE consists of two kinds:

- Exergy stocks in the natural environment
    - Water
    - Fossil fuels
- Flows of exergy that powers the natural ecosystems.

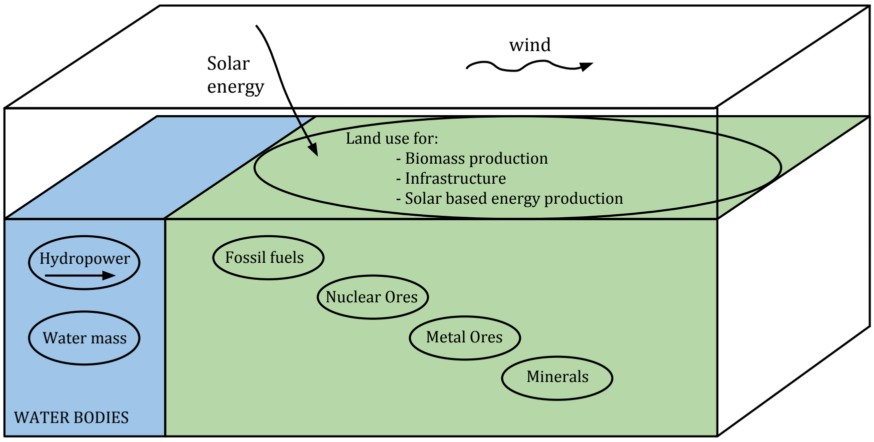


Figure 4.1 Schematic representation of Impact Categories (from [111]**)**

Within this method eight are the categories of assets taken from natural environment that can be distinguished [111]:

- Fossil fuels
- Water resources
- Renewable resources
    - Wind
    - Hydropower
    - Solar
- Nuclear energy
- Metal ores
- Minerals and mineral aggregates
- Land resources
    - Biomass
    - Land occupation
- Atmospheric resources.

Between the above listed categories the '*land occupation*' can be accounted as the most innovative. This category accounts for the impossibility for the natural ecosystem to make use of the solar exergy flow incident on the land [110], which could be used for photosynthesis in plant growth. And since the solar influx drive the sustainability of the ecosystem; also land use has an impact on the environment. Land occupation impedes the exergy of solar irradiation to be used in photosynthesis in plant growth [110].

Be aware, the category 'renewable resources' does not comprise solar energy and biomass to avoid double counting. [110]

4.4.3 Application

In [110], it is said that this approach will help mankind to sustainably using natural resources, because it reflects the chemical price the environment pays for the withdrawals of the industrial society.

In literature [110], the analysis of energy production systems with CEENE method showed that the major exergy source of production comes from the same energy carriers utilized. Only when solar technologies are considered the land occupation has a substantial contribution to the total exergy. In the analysis of material production, exergy from non-renewable energy sources (fossil fuel and nuclear) exhibits a large share in the CEENE score.

Finally, it can be underlined that CEENE allows accounting for different natural resources consumptions, from nonrenewable resources, renewable resources, atmospheric and water resources, and land use. The best solution would be to combine CEENE with an emission-oriented assessment methodology, so as to consider the impact of resource input as well as emission output.

4.4.4 Additional Notes

CEENE, in comparison with resource indicators like cumulative energy demand (CED) and CExC, offers more detailed information on resource demand. CED only accounts for resources but neglects non-energetic resources like metals, minerals, and water. CExC is more comprehensive then CED, considering the mentioned non-energetic resources, but does not consider the land occupation. For those reasons CEENE can be considered the most comprehensive resource indicator, since it evaluates both energetic and non-energetic resources, and land occupation [110].

CExC and CEENE are conceptually, qualitatively and quantitatively different. The former estimates the exergy removed from nature and transferred into the industrial society, the latter evaluates the total exergy natural system is deprived of. In case of biomass, CEXC assigns an exergy value to biomass, while CEENE considers the exergy deprivation from the natural environment due to land occupation during biomass growth.

The exergy of metals in CExC is computed as the whole metal ore enters into the technosphere, CEENE accounts only for the metal-containing minerals of the ore, since the tailings from the beneficiation are often not chemically altered when deposited [110].

The qualitative aspect is just a matter of different literature sources, which lead to some discrepancies [110].

Finally, the main innovation of CEENE as indicator is that allows quantifying the extraction of exergy that could have been, or could be, useful for natural ecosystems.

4.4.4.1 Check for Double Counting

Solar-based technologies and agricultural and forestry products require land use, whereas at the same time the renewable products are considered.

Land occupation means solar exergy use whereas the renewable products represent part of this same solar exergy. Setting correct boundaries eliminates double counting: as soon as forestry and agriculture are intensive they become part of the industrial metabolism. This means that, they make use of land within the industrial system depriving the natural ecosystem from solar exergy. The same is valid for solar-based technologies. Their products are no longer purely natural and should be considered as any other products being marketed within the industrial society. [110]

4.4.4.2 System Boundaries

The definition of system boundaries is crucial to pinpoint what flows or stocks have to be considered or excluded, so it has to be unambiguous what passes through the industrial ecosystem/natural environment boundary. Any amount of exergy unavailable to sustain natural processes because it has been used by industry has to be taken into account. [110]

This means that, for solar energy, the fraction that is deprived from the first trophic level necessary for sustaining natural processes and cycles, is taken into account. In case of land use, it is considered that the natural ecosystem, and in particular again the first trophic level, can no longer make use of the solar exergy flow that is insolated onto this land. From a thermodynamic point of view, this solar influx is the driving force for the natural ecosystem to sustain itself.

4.4.4.3 Reference Environment

For the feedstock this method uses Szargut's reference environment, where reference temperature and pressure are respectively 298K and 1 atm, while composition is slightly different due to an updated reference compound for aluminium [109].

4.4.4.4 *Exergy Calculation of Energy and Materials*

In the exergy calculation by Dewulf et al. [110] 184 reference flows are considered for the resources extracted out of the ecosystem. The data are needed to compute the conversion factors X which quantify the CEENE of each impact category, and it is defined as the exergy content of a considered reference flow per unit of the reference flow (MJ_{ex}/kg, MJ_{ex}/MJ, MJ_{ex}/Nm^3, MJ_{ex}/m^2a).

The calculation of X factor for metals extracted from minerals [110] requires a brief explanation. The formula, from [110], is

$$X = \frac{\sum_i v_i e_{ch,i}}{MW_{element}} \tag{4.8}$$

Where $MW_{element}$ is the molar weight of the element, v_i the mole fraction of the mineral that will be mined for one mole of the element, and $e_{ch,i}$ is the chemical exergy of the *i*th mineral.[2]

And the CEENE for a product (or service) *j* is calculated as the the sum of the products of the X factors (some in Table 4-2) of the reference flow and the cumulative amount a_{ij} from the reference flow *i* necessary to obtain the product *j*.

$$CEENE_j = \sum_i \left(X_i \times a_{ij} \right) \tag{4.9}$$

---

[2] For example, for aluminum production the ore bauxite is extracted. The main minerals in this ore are boehmite ($Al_2O_3.H_2O$), gibbsite ($Al_2O_3.H_2O$) and diaspore ($Al_2O_3.3H_2O$). They are assumed (due to lack of more detailed information) to deliver equal shares (1/3) of the aluminum moles in the ore extraction. The fractions v_i are then all 1/6, as each mineral molecule incorporates two aluminum atoms. The X value for the aluminum reference flow is then (1/6*31.2+1/6*24.6+1/6*21.0)/26.98 = 0.474 MJ_{ex} of exergy per kg aluminum atoms (bound in minerals) extracted.

4.4.4.5 *Results*

Table 4-2 X factors used in CEENE method

Category	*Value*	*Unit*	*Note*
Fossils			
Natural Gas	38.28	MJ$_{ex}$/Nm^3	European Natural Gas Mix
Crude Oil	46.2	MJ$_{ex}$ /kg	NCV=43.2 MJ/kg and beta=1.07
Sulphur, in ground	18.94	MJ$_{ex}$ /kg	Elemental Sulphur
Peat	10.21	MJ$_{ex}$ /kg	GCV=9.9 MJ/kg and beta=1.031
Coal	10.3 ÷ 19.7	MJ$_{ex}$ /kg	'Brown coal' ÷ 'Hard coal'
Metal Ores			
Aluminium	0.47	MJ$_{ex}$ /kg	Aluminium, 24% in bauxite, 11% in crude ore, in ground
Copper	15.8	MJ$_{ex}$ /kg	
Iron	0.362	MJ$_{ex}$ /kg	Iron, 46% in ore, 25% in crude ore, in ground
Silver	3.28	MJ$_{ex}$ /kg	Silver, 0.01% in crude ore, in ground
Zinc	11.4	MJ$_{ex}$ /kg	Zinc 9%, in sulphide, Zn 5.34% and Pb 2.97% in crude ore, in ground
Nuclear Energy	$4.69 \cdot 10^5$	MJ$_{ex}$ /kg	Uranium Ore, in ground
Biomass	22.42÷22.28	MJ$_{ex}$ /kg	Softwood ÷ Hardwood
Land Occupation	68.14	MJ$_{ex}$ /(m^2·a)	
Renewable Exergy Flows			
Hydropower	1.253	MJ$_{ex}$ /MJ	Potential Energy Stock in barrage water
Geothermal Energy	0		
Wind Power	4	MJ$_{ex}$ /MJ	
Solar-Based Tech.	68.14	MJ$_{ex}$ /(m^2·a)	
Minerals and Mineral Aggregates			
Basalt	0.31	MJ$_{ex}$ /kg	
Calcite	0.184	MJ$_{ex}$ /kg	
Granite	0.09	MJ$_{ex}$ /kg	
Sand	0.031	MJ$_{ex}$ /kg	
Air Resources			
CO_2, in air	0	MJ$_{ex}$ /kg	
Water Resources	50	MJ$_{ex}$ /m^3	Lake, river, in ground well

Metal Ores: ore extraction, beneficiation and processing are the steps that the petl production consists in. During the extraction phase the crude ore is obtained together with overburden, which will not be further processed. Ore concentrate, together with tailings, is the result of the beneficiation of crude ore. Tailings may be chemically transformed or grinded. Processing of concentrated ore, diversely to the previous ones, destroys the ore mineral and generates wastes. Therefore exergy is accounted only for the minerals, which contains the target metals, while overburden and tailings exergy content is not used since they will return to the environment and potentially could be used in future.

Nuclear Energy: briefly, the steps are mining, milling, conversion, enrichment, fuel element production, nuclear electricity production, burnt fuel reprocessing, and mixed oxide (MOX) fuel element production. Burnt fuel conditioning, waste storage and depleted U-238 storage are not included in the analysis, because they do not affect the amount of atoms that is actually consumed by fission [110].

Land Occupation: except for "occupation, pasture and meadow, extensive" [110], all kinds of land occupation detract natural ecosystem from the solar exergy that supports the natural cycles. Dewulf et al. [110] calculated a solar exergy flow of 34071 $GJ_{ex}/ha \cdot a$ counting on 2.78 $kWh/m^2 \cdot day$ [3] and a ratio exergy to energy of 0.9327 . The fraction used by marine systems is neglected because it is two orders of magnitude lower than the natural land ecosystems. In the latter case, the photosyntetically active part (PAR) is only 45%, but due to reflection only 40% of the overall solar exergy is used by the natural ecosystem. In the end 2% is the metabolization efficiency with half of the exergy dissipated through respiration, so during one year the exergy value of land use is 681.4 $GJ_{ex}/ha \cdot a$, which correspond to 14.8 ton oil equivalent[4].

Renewable Exergy Flows (Hydropower, Geothermal Energy, Wind Power, Solar-Based Technologies): only the fraction of exergy useful for natural ecosystems is accounted for into this methodology. The total potential exergy extracted by hydropower is considered, as so for the total kinetic exergy extracted from wind by windmills. The case of geothermal energy is split in two: if the low temperature heat is regarded as environmental heat, it does not have any exergetic value; while, when deep geothermal power plants will take the scene this asset would have a value. Now the "energy, geothermal" value is set to zero. When solar-based technologies are considered they should bear both land use and solar irradiation, but to avoid double counting only exergy extraction from the former is accounted for.

---

[3] Average irradiation for Western European conditions

[4] Exergy value of 1 ton crude oil is 46.2 MJ_{ex}

Minerals and Mineral Aggregates: these flows are considering the average composition of minerals, and the uncertainty of the calculation results can be very high. But since this exergy values are so small, the overall results and their validity shouldn't be affected.

4.5 Extended Exergy Accounting (EEA)

4.5.1 Definition

The Extended Exergy Accounting, in short EEA, is a method that is an extension of CExC [81], it has the singularity to take into account all externalities using exergy. With EEA it is possible to assess the cost of a commodity in terms of primary resources.

Extended Exergy Accounting is an incorporation of aspects of life cycle analysis, cumulative exergy analysis, extended exergy analysis and complex systems analysis. The term 'extended' is used to bring to mind the inclusion of non-energetic cost and externalities. [112]

EEA is based on two assumptions [113]:

- The cumulative exergy content of a good or a service is equal to the sum of the raw exergy of the original constituents that form the input to the production process plus a properly weighted sum of all the exergetic inputs into the process itself.
- Non-energetic externalities, Capital and Labor can also be expressed in exergetic terms, in a way that they have an exergetic equivalent resulting from global system balances.

Since exergy seems to match with economic values [112], EEA pursues a comparison between the economic cost function and the exergetic one, highlighting on one hand the similarities on the fact that both costs evaluate the consumption of resources due to the production, while on the other hand that differences in the structure of the functions may lead to different optimal design points.

4.5.2 Impact categories

In EEA methodology the categories considered to have an impact on the environment are the general inputs of a process: energy supply, raw materials, human labor and capital, plus the environmental damage of effluents.

The energy supplied to the process is converted into the correspondent exergy.

The raw materials stream possesses as exergy value the cumulative exergy content that results from the sum of its physical exergy and of all the net exergy inputs received during its past processes (e.g. extraction, transportation, etc.) [112].

Human Labor is considered as the product of the society, so that its exergy equivalent is strictly connected with the resources absorbed by the same society.

Capital has an exergy value purely related to the monetary circulation within a society.

The exergy value of environmental damage of effluents is linked to all the exergetic inputs needed for the treatment processes of emissions or wastes flowing out of the system. These treatments take the effluents to a quasi-zero exergy value, later the surrounding environment will bring them down to the equilibrium.

4.5.3 Application

This method can be employed to compare homogeneously heterogeneous quantities. Therefore, allows to compare different socio-economic pictures by referring them to a common basis related to the consumption of primary resources [81].

4.5.4 Additional Notes

Like the economic cost function (4.10), which takes into account the capital, labor, fuel and environmental effects of pollutants, the extended exergy considers monetary capital, labor, heat and power, materials, and environmental remediation cost [49].

$$c_{eco} = f\left(K, L, E, M, O\right) \tag{4.10}$$

$$\mathrm{ee} = f\left(K, L, E, M, O\right) \tag{4.11}$$

Where:

- K — monetary capital
- L — labor
- E — any kind of energy flow
- M — material
- O — environmental remediation.

The extended exergy of a commodity ($\mathrm{EE}_{\mathrm{commodity}}$) “quantifies the number of Joules of primary exergy that were cumulatively used to produce that commodity, are being used over its operating life, and will be used for its disposal”[113], and can be formulated as

$$\mathrm{EE}_{\mathrm{commodity}} = \mathrm{CExC} + \mathrm{EE}_{\mathrm{K}} + \mathrm{EE}_{\mathrm{L}} + \mathrm{EE}_{\mathrm{O}} \tag{4.12}$$

Where the CExC of the commodity corresponds to the initial exergy of material inputs increased with all the exergetic equivalents of the various energy inputs used in the production process. The other term are explained here below.

The term EE_O stands for the exergy equivalent of environmental costs [38], since from a process can be produced pollutants. For a generic system 'pollutants' are considered its effluents, which hardly can be in equilibrium with the environment. The exergy equivalent of environmental cost counts for the extra-exergy requirements needed to build and sustain a facility that can abate the exergy content of the effluents, look at figure.

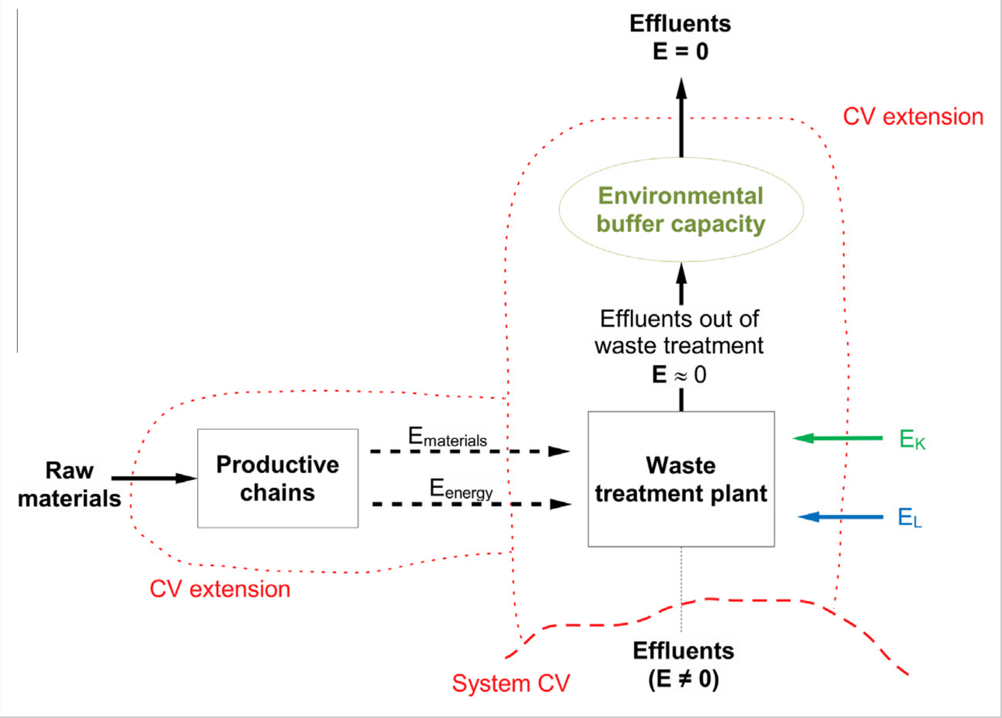


Figure 4.2 Addition of a virtual waste treatment plant to compute the environmental costs of pollutants [38]

The term EE_L correspond to the exergy content of the labor needs in the production of the commodity. It is obtained through the exergy equivalent of labor (ee_L), which is calculated as

$$\mathrm{ee}_L = \frac{\alpha \cdot B_{in}}{N_{wh}} \qquad (4.13)$$

Where

- α is the 'first econometric coefficient', representing the fraction of primary exergy absorbed by the society and converted into labor

- B_{in} is the net exergy globally absorbed by the considered society
- N_{wh} is the total number of workhours within the society

The ‘capital externality’ is the term EE_K, which is obtained with the ‘exergy equivalent of the capital’, defined by the second postulate of EEA that states: “the amount of exergy required to generate the net monetary circulation within a society is proportional to the amount of exergy embodied into labour” [114].

$$\mathrm{ee}_{\mathrm{K}} = \frac{\alpha \cdot \beta \cdot B_{in}}{M2} \tag{4.14}$$

where

- β is the ‘second econometric coefficient’, which indicates the capacity of a society to generate monetary circulation in addition to wage compensation and is the ratio between financial activities (M_F) and gross cumulative wages (S): $\beta = M_F / S$
- M2 is a monetary aggregate that comprise currency in circulation, ‘overnight deposits’ plus deposits with original maturities of up to two years and deposits redeemable at notice of up to three months [38]

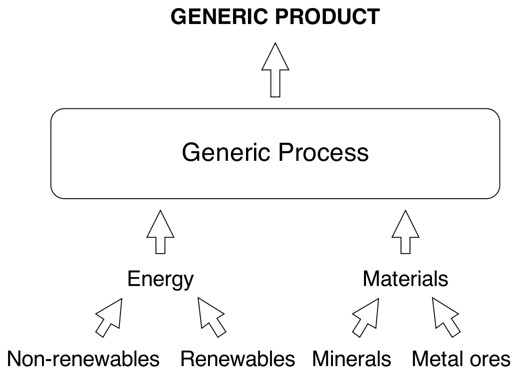
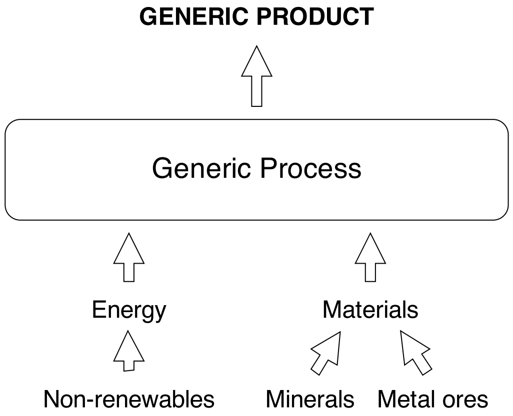
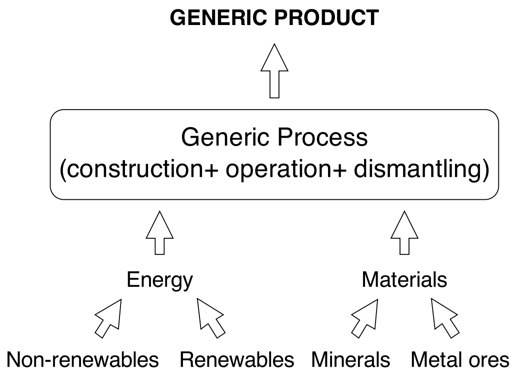
EEA owes several of its concepts to the previous theories:

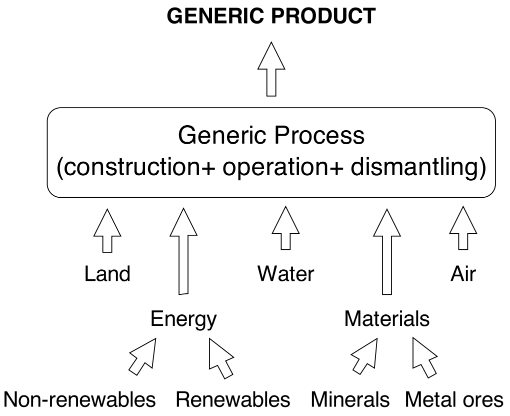
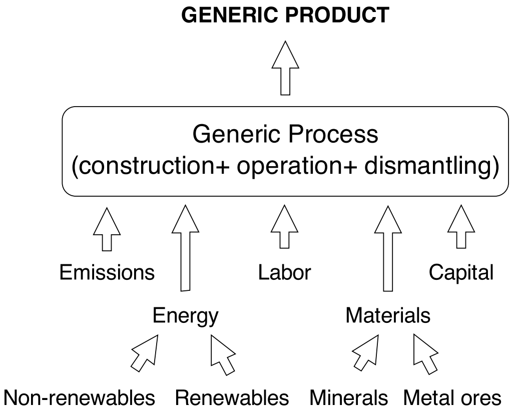
- From LCA, EEA adopted a life-cycle type of approach for each commodity, starting from the extraction of primary sources and ending with the recycling of wastes.
- As in classical Exergy Analysis, EEA uses exergy as a measure of the energetic content of every material and immaterial flow directly or indirectly used in a process.
- As in Cumulative Exergy Content, EEA calculates the exergy “embodied” in a product by keeping track of all of the exergy inputs and outputs in the production chain.
- From Emergy Analysis, EEA took the concept of attributing a resources-based cost to “external” produc- tion factors (human labour and capital).
- From Embodied Energy Analysis, EEA borrowed the treatment of environmental externalities. [81]

4.6 Critical analysis and future developments

4.6.1 Resuming table

Table 4-3 Brief overview of the exergy-based paradigms

<table>
<tr><th>Paradigm</th><th colspan="2">Impact categories</th></tr>
<tr><td>CExC</td><td>Energy
• *Non-renewables*
  - *Fossil fuels*
  - *Nuclear*
• *Renewables*
  - *Wind*
  - *Solar*
  - *Geothermal*
  - *Hydropower*
  - *Biomass*
Materials
• *Metal ores*
• *Minerals*
• *Water*</td><td> </td></tr>
<tr><td>TEC</td><td>Energy
• *Non-renewables*
  - *Fossil fuels*
  - *Nuclear*
Materials
• *Metal ores*
• *Minerals*</td><td> </td></tr>
<tr><td>ELCA</td><td>Energy
• *Non-renewables*
  - *Fossil fuels*
  - *Nuclear*
• *Renewables*
  - *Wind*
  - *Solar*
  - *Geothermal*
  - *Biomass*
Materials
• *Metals*
• *Minerals*</td><td> </td></tr>
</table>

CEENE	Energy • Non-renewable - Fossil fuels - Nuclear • Renewable - Solar - Geothermal - Wind - Hydropower Materials • Metal ores • Minerals Land resources • Biomass • Land occupation Water resources Air resources	
EEA	Energy • *Non-renewables* - *Fossil fuels* - *Nuclear* • *Renewables* - *Wind* - *Solar* - *Geothermal* - *Hydropower* - *Biomass* Materials • *Metal ores* • *Minerals* • *Water* Labor Capital Emissions	

4.6.2 Criticalities

In Table 4-4 some differences among the analysed paradigms are showed. It appears clear that, even if there is a will in assessing resource consumption, for each characteristic there is lack of total accordance.

Table 4-4 Brief list of methods characteristics

Methods	Natural Resources Included	LCA approach	Boundaries	Geographical consistency	Externalities	Reference Environment
CExC	Funds + Deposits	No	Industrial society	Global	Environmental	Szargut
TEC	Deposits	No	Industrial society	Local	Environmental	Szargut
ELCA	Funds + Deposits	Yes	Industrial society	Global	Environmental	Szargut
CEENE	Funds + Deposits	Yes	Interface environment/ industrial society	Global	Environmental	slightly different from Szargut
EEA	Funds + Deposits	Yes	Industrial society	Local	Environmental, economic and social	Szargut

4.6.3 Advantages and drawbacks

4.6.3.1 Advantages

CExC

- “It can consider material and energy resources” [35]

TEC

- Considers only the natural resources that are exhaustible [105].

CEENE

- “Account for only the used exergy, which for sunlight to biomass is about 2%” [35]
- Evaluates both energetic and non-energetic resources, and land occupation [110].
- Does not commit double counting when biofuels are considered [51]

- Addresses the shortcoming of confusing exergy loss in ores with exergy loss in the minerals that actually contain the metals being exploited [51].

EEA

- "Includes the role of human labor and activities" [35]
- Includes social, economic and environmental externalities using the same numeraire [38]

4.6.3.2 Drawbacks

CExC

- Renewable resources "tend to dominate" over the non-renewables, when "considered together" and "the calculated metrics can be misleading" [35][115]. "This is due to the inability of CExC to account for quality differences between resources" [35]
- Involves no monetary calculations [49]
- No clear system boundaries definition exists "to determine where the regression in CExC calculation should be stopped" [38]

TEC

- It considers only the non-renewable resources

CEENE

- "Does not account for the role of nature" [35]

EEA

- The database is still not sufficiently accurate [38]
- The results of EEA depends on the local and temporal context in which the system operates [38]
- When CExC values are used no addition of labour or other externalities are made to correct such values [38]
- It does not define a universal abatement system to avoid miscalculation when computing the effluents exergy equivalent
- The definition of exergy equivalent of labour is not considering the employment rate of a country but only its workers [38]
- The definition of equivalent of monetary capital does not guarantee that real capital circulation is taken into account [38]

4.6.4 An alternative paradigm for primary resource depletion assessment

Consequently to the previous different paradigms examination, an alternative direction is here proposed. The basic idea takes is based on the methodology of TEC and includes also the labor, like in the EEA. An alternative method to calculate the exergetic cost of labor and it is formalize in its first approach in the following sections.

4.6.4.1 Definition

The alternative paradigm is here referred to as *ETEC*, meaning *Extended Thermo Ecological Cost thus being* clearly inspired by the approach of EEA [112] and the Thermo Ecological Cost [104].

4.6.4.2 Impact categories

The ETEC considers as impact categories:

- Non-renewable energy resources;
- Mineral resources;
- Labor.

It result that the same impact categories of TEC are listed above, but *labor* is also taken into account.

4.6.4.3 Mixing TEC with only labor from EEA

During this work, it has been unveiled that resource consumption is a very complex problem, but if we focus just on the depletion of natural assets, then only the exhaustible resources has to be accounted. For this reason the TEC method has been chosen.

From the EEA [112] it has been taken the concept of accounting for labor, while monetary capital or emissions have not been considered. The latter does not have a single calculation method and therefore, if the emission abatement system changes, no computation can be replicated with the same results. The choice of not considering the monetary capital is made on the hypothesis that money exists only to facilitate the exchange of things.

4.6.4.4 Accounting for labor in ETEC

To explain how to take into account 'labor' inside the exergetic cost function a general description and brief analysis of a general society has to be given.

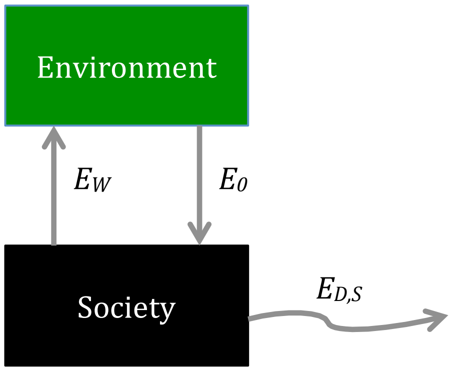


Figure 4.3 Schematic view of the exergetic interactions between Society and Natural Environment

Imagine a society like a black box that can interact only with the natural environment and all the flows exchanged are measured with exergy.

Looking at Figure 4.3, it is evident that all the natural resources flow in the black box having a certain amount of exergy (E_0), after being processed, flow out the black box, with a lower amount of exergy (E_W). During this exchange some exergy has been destroyed, and so an exergy balance can be written:

$$E_0 = E_{D,S} + E_W \tag{4.15}$$

Where E_0 is the incoming flow into the society, $E_{D,S}$ is the exergy destroyed during the processes that happen in the black box, and E_W is the exergy content of the flow that exits the box.

Let's make a semi-realistic hypothesis that the wastes stay within the society, and so there is no flow coming back into the natural environment, and the exergy balance will become

$$E_0 = E_{D,S} \tag{4.16}$$

Said that, one can think that a society needs resources to sustain itself, but since the goods and services circulate within it they cannot be the product of a society. Opinion of the author is to consider the hours that members of the society can spend for living, and not for work, as the real and only product of a society. Taking one year as basis:

$$H_T = 8760 \cdot N_P \tag{4.17}$$

$$H_W = h_{work} \cdot N_W \tag{4.18}$$

$$H_L = H_T - H_W \tag{4.19}$$

Where:

- H_T is the cumulative amount of hours available to a society,
- N_P corresponds to the population,
- h_{work} is the number of hours of work in a year,
- H_W is the cumulative working-hours of the society,
- N_W is the number of workers of the society, and
- H_L is the cumulative number of hours that society does not spend working.

As demonstrated by Szargut and Stanek [116], no exergy is physically contained in the working hours. But it could be added that a non-zero exergy cost can be computed for the hours of life, and assign this exergetic cost to the working-hours shall help to calculate the total exergetic cost of any commodity.

Making use of the previous formulations, the *average exergy cost of one hour of life for a human being* in a certain society can be defined as:

$$c_h = \frac{E_0}{H_L} \tag{4.20}$$

To maintain certain validity when applied to process analysis, the discussion written previously may need to be examined within a microscopic view.

Imagine that the society's black box of Figure 4.3 is now unveiled, and, as showed in Figure 4.4, there is a simple society made of a sector 'B', which is the 'domestic sector', and just two generic 'resource-processing' sectors 'a' and 'b', where natural resources are processed and delivered to the domestic sector. It is not relevant what kind of products are the outputs of sectors 'a' and 'b', but it is important that the society consumes those goods, which come from the processing of natural resources.

The input of the domestic sector are the flows of goods $E_{1,a}$ and $E_{1,b}$ respectively coming from the resource-processing sectors 'a' and 'b', whilst the outputs consist in 'working hours' (H_W) plus 'nonworking-hours' (H_L). Notice that both the outputs of domestic sector have no exergy content, but while the nonworking hours help producing nothing, a fraction of the working hours goes into 'a' ($H_{w,a}$) and the remaining fraction ($H_{w,b}$) goes into 'b'. In this way the working hours can be considered inputs of the resource-processing sectors together with the natural resources extracted from the environment.

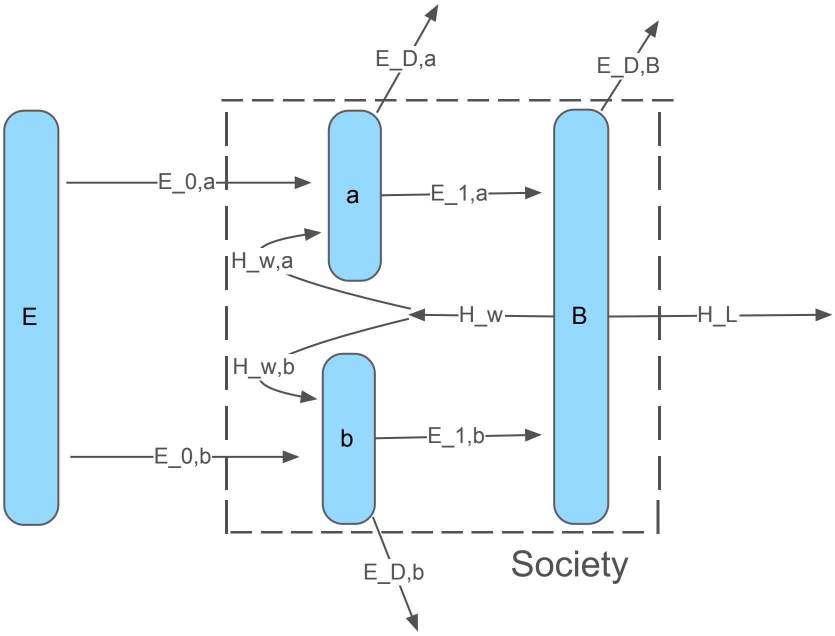


Figure 4.4 Schematic representation of society. Environment (E), domestic sector (B), resource processing sectors (a) (b)

Referring to Figure 4.4, different exergy balances can be written: for the entire society (4.21); for both resource-processing sectors (4.22) (4.23); and for just the domestic sector (4.24). In each balance the exergy destruction is considered and denoted with the subscript 'D'.

$$E_0 = E_{0,a} + E_{0,b} = E_{D,a} + E_{D,b} + E_{D,B} \tag{4.21}$$

$$E_{0,a} = E_{1,a} + E_{D,a} \tag{4.22}$$

$$E_{0,b} = E_{1,b} + E_{D,b} \tag{4.23}$$

$$E_{1,a} + E_{1,b} = E_{D,B} \tag{4.24}$$

Also exergetic cost balances can be written: for the entire society (4.25); for both resource-processing sectors (4.26)(4.27); and for just the domestic sector (4.28).

$$\mathrm{C}_{\mathrm{HL}} = \mathrm{E}_{0,\mathrm{a}} + \mathrm{E}_{0,\mathrm{b}} = E_0 \tag{4.25}$$

$$\mathrm{C}_{1,\mathrm{a}} = \mathrm{E}_{0,\mathrm{a}} + \mathrm{C}_{\mathrm{HW,a}} \tag{4.26}$$

$$\mathrm{C}_{1,b} = \mathrm{E}_{0,b} + \mathrm{C}_{HW,b} \tag{4.27}$$

$$\mathrm{C}_{HW} + \mathrm{C}_{HL} = \mathrm{C}_{1,a} + \mathrm{C}_{1,b} \tag{4.28}$$

Therefore, using the balance (4.25), it results

$$\mathrm{c}_h \cdot H_L = \mathrm{E}_0 \Rightarrow c_h = \frac{E_0}{H_L} \tag{4.29}$$

Using the term c_h, the other balances can be reformulated as follows

$$\mathrm{C}_{1,a} = \mathrm{E}_{0,a} + \mathrm{c}_h \cdot \mathrm{H}_{W,a} \tag{4.30}$$

$$\mathrm{C}_{1,b} = \mathrm{E}_{0,b} + \mathrm{c}_h \cdot \mathrm{H}_{W,b} \tag{4.31}$$

$$\mathrm{c}_h \cdot \mathrm{H}_W + \mathrm{c}_h \cdot \mathrm{H}_L = \mathrm{C}_{1,a} + \mathrm{C}_{1,b} \tag{4.32}$$

So (4.32) becomes

$$c_h\left(H_{W,a} + H_{W,b}\right) + c_h \cdot H_L = E_{0,a} + E_{0,b} + c_h \cdot H_{W,a} + c_h \cdot H_{W,b} \tag{4.33}$$

$$\mathrm{c}_h \cdot \mathrm{H}_L = \mathrm{E}_{0,a} + \mathrm{E}_{0,b} \tag{4.34}$$

Which means that the exergetic cost of labor is associated only with the consumption that the domestic sector has, and that it can be used to account labor in an exergy cost function to evaluate the exergetic cost of goods or services.

Based on what affirmed before, one could try to analyse what can happen to the value of c_h when, as extreme situation, there are no working hours. If no one works,

$$H_W = 0 \tag{4.35}$$

From (4.19), it results

$$H_L = H_T \tag{4.36}$$

Viz

$$c_h = \frac{E_0}{H_T} \tag{4.37}$$

And since no working hours are generated from the domestic sector, the exergetic cost balances can be formulated again (society (4.38), sector ‘a’ (4.39), sector ‘b’ (4.40), domestic sector (4.41)(4.42)):

$$\mathrm{C_{HL}} = \mathrm{E_{0,a}} + \mathrm{E_{0,b}} = \mathrm{E_0} \tag{4.38}$$

$$\mathrm{C_{1,a}} = \mathrm{E_{0,a}} + \mathrm{c_h} \cdot 0 \Rightarrow \mathrm{C_{1,a}} = \mathrm{E_{0,a}} \tag{4.39}$$

$$\mathrm{C_{1,b}} = \mathrm{E_{0,b}} + \mathrm{c_h} \cdot 0 \Rightarrow \mathrm{C_{1,b}} = \mathrm{E_{0,b}} \tag{4.40}$$

$$\mathrm{c_h} \cdot 0 + \mathrm{c_h} \cdot \mathrm{H_T} = C_{1,a} + C_{1,b} \Rightarrow \mathrm{c_h} \cdot \mathrm{H_T} = C_{1,a} + C_{1,b} \tag{4.41}$$

$$\mathrm{c_h} \cdot \mathrm{H_T} = \mathrm{E_{0,a}} + \mathrm{E_{0,b}} = \mathrm{E_0} \tag{4.42}$$

Accordingly, it appears that, even if the working hours were null, the system could continue to run.

On the other extreme, another reasoning could be supposing that, absurdly, the society does not generate any living or ‘spare time’ hours, so

$$H_L = 0 \tag{4.43}$$

In this case every human being spend each hour of his life working in the resource processing sectors.

In addition, the c_h can be computed by different paradigms, if the analyst wants to include also the labor category among the impact categories of another methodology. But keep in mind that depending on the paradigm that is used, the value of c_h can vary. In any case, in this work, no other paradigm has been applied to calculate the variation of c_h.

5 An exergy cost accounting application

5.1 Electric wire case study

The case study undertaken in this work is a simple electric wire that is part of an electric circuit to power a generic user. The aim of this particular study has been analysing how the resources consumption varies changing the diameter of the wire, using a process analysis approach.
This work can be described in two main steps:

1. Generic model creation;
2. Paradigm application.

Finally there is the analysis of the results.

5.1.1 Generic model creation

The model used has been entirely created on excel using different data sources (see Appendix B).

The modelling can be separated in two frameworks: time and space. The first is just the definition of the phases of the wire life that has to be considered: only construction and operation has been taken into account; dismantling has been omitted in this study due to lack of data. The second framework of the modelling is quite more complex then the former, and will be explained here below.

The main system of the model is the cable, and it has the energy supplied to the user as its only output. The inputs to the electric cable come from the other units. The model contains different units interconnected among each other.

The energy is supplied using an Electricity Production System (‘EPS’ in the scheme) that in this case is a Gas Turbine. This latter is fuelled with natural gas coming from the Fuel Extraction & Production System (‘FUEL’ in the scheme).

The material that will appear only in the construction phase is copper, so the cable is thought being supplied by the “components factory” system (‘FACT’), which uses only electricity from the EPS unit for its process. The copper entering into the factory comes from the “Metal Ore Extraction & Production” units (‘ORE’), which it is also supposed to use only electrical energy from the EPS unit for its processes.

All this units have a generic list of inputs, some of which have been neglected for the calculation:

- Energy;
- Material;

- Human labor;
- Land;
- Emissions & Wastes;
- Capital.

In the model, the size of the wire diameter has been chosen as the only variable. Also other parameters can be changed, but in this particular case there was no will in demonstrating how different parameters affect the optimal design.

For the construction phase the electrical cable is supposed to need:

- Energy to be transported and installed;
- Copper (Material) that actually the wire is made of;
- Human labor to be transported and installed;
- Land that is being occupied during the installation;
- Emissions released during installation and transportation;
- Taxes (Capital) that have to be considered when the cable is bought.

The needs of the other units depend on the above listed energy and material requirements.

5.1.2 Main system configuration

For the main system two components should be considered:

- The future user facility, and
- The cable.

For the former, the power to be supplied (P_{user}) and the internal resistance have been set, respectively, to 1000 W and 10 Ω. No other information was considered necessary.

For the cable the three could have been the variables:

1. Diameter
2. Length
3. Material

The second has been fixed to 20 meters, while for the third, *copper* has been chosen (physical characteristics in Table 5-1). Finally the diameter has been selected as the only variable of the main system.

Table 5-1 Copper physical characteristics

Resistivity	Density
Ω·m	**kg/m³**
1,68 · 10⁻⁰⁸	**8940**

The power supplied P_{el} to the whole main system is:

$$P_{el} = P_{user} + P_{loss} \tag{5.1}$$

Where P_{loss} is the electrical power lost due to dissipations.

Life-cycle approach

For the construction phase the inputs used have been:

- Energy, supposed electrical, for transportation and installation of the cable;
- Amount of material required, depending on the variable diameter;
- Land used corresponds to the cross-sectional surface taken considered along longitudinal direction multiplied for the duration of the installation and divided by the hours in a year;
- Human labor is the time a worker take to install the cable;
- Monetary capital corresponds to the taxes applied to the price of the cable.

Notice that the land use is accounted as if a portion of soil has been occupied for one year. For this reason, the surface is multiplied for the time percentage the installation lasts.

For the operation phase the inputs were:

- Electrical energy supplied to the main system;
- No materials for connections;
- Land occupied by the cross-sectional surface in longitudinal direction;
- Time an employee takes to monitor and control the main system;
- Tax over the land used.

5.1.3 Secondary systems configuration

What are called ‘secondary system’ represent all the single or aggregate systems that process the final inputs of the main system. The so-called secondary systems are listed below, and will be described in the following subsection:

- Electricity production system (EPS)
- Fuel extraction and production (FUEL)
- Component’s factory (FACT)
- Metal ore extraction and production (ORE)

5.1.3.1 Electricity Production System (EPS)

The electricity production system has been assumed to be a *gas turbine*, working always in optimal design conditions, never off-design. The EPS supplies all the energetic needs of the unit in this model, except the ‘FUEL’ one, since electricity is supposed to be the only energy carrier they use.

The energy conversion efficiency η_{EPS} is supposed to have a value of 30%, and then, the incoming energy flow of gas results from (5.2).

$$P_{EPS} = \frac{P_{el}}{\eta_{EPS}} \tag{5.2}$$

Life-cycle approach

For the *construction* phase the outputs of the EPS were:

- Electricity supplied to the transport and install the cable;
- Electricity supplied to manufacture the cable;
- Electricity supplied to extract and produce the copper from ore.

Whilst the inputs of the *construction* phase were the same of the EPS *operation* phase:

- Energy of the natural gas needed to supply the electricity to the main system;
- Land occupied by the gas turbine power plant;
- Labor time needed to control and monitoring operations;
- Taxation over land occupation.

No materials are considered for connections, and the building materials of the gas turbine are not considered because of the hypothesis that the gas turbine will work for more than the time required by the main system.

5.1.3.2 Fuel extraction and production (FUEL)

The system called FUEL is a macro-aggregate system, which includes all the processes that contribute in the extraction and production of fuel, in this case the natural gas. This system has direct interface with the deposit of natural gas in the environment, and for simplicity it has been assigned an efficiency of fuel production η_{FUEL}.

Life-cycle approach

In general, its inputs were:

- Energy possessed by the crude fuel at the extraction;
- Land occupied by all the plants required to extract and produce the natural gas needed;
- Labor time necessary to process the natural gas, from its extraction to its production;
- Taxation over the land occupied.

Its output during both the *construction* and the *operation* phases was:

- Energy of the natural gas supplied to the EPS.

5.1.3.3 Component's factory (FACT)

The system called FACT has the scope of producing the copper wire. It has been assumed that some material get lost during the manufacturing process, so that the efficiency η_{FACT} is not unitary, and, for hypothesis, is set to *0.9*.

<u>*Life-cycle approach*</u>

The FACT system is assumed to function only to supply the cable during the *construction* phase, while no material is required for the *operation* phase.
The inputs were:

- Energy required to manufacture the cable;
- Pure copper, as only material input;
- Fraction of land occupied by the factory attributable to the production of a single cable;
- Labor time required to produce a cable;
- Taxation over land occupation.

5.1.3.4 Metal ore extraction and production (ORE)

The ORE system is, similarly to FUEL, a macro-aggregate unit, where all the processes of extraction and, in general, production of metal ore are included. This system has a pure metal production efficiency, which has been set to *0.9*, just for hypothesis. Its output is the pure copper that enters in the FACT unit.

<u>*Life-cycle approach*</u>

Since the system FACT operates only during the *construction* phase, the ORE unit was not required to function neither during the *operation* phase.
The assumed inputs were:

- Energy required to extract ore and produce pure copper from it;
- Ore extracted from the copper mine;
- Land occupied by all the plants that extract and process the copper ore;
- Labor time to obtain pure copper, taking into account all the processes involved in mining and copper production;
- Taxation over the mines and the land occupied by the processes, referred to the amount of extracted ore.

5.1.4 Paradigms application

The objective of applying different paradigms has been to find out how the optimal size of the wire diameter changes between each of these methods. In order to do that, conversion factors has been used to convert into exergy values the inputs of the control volume.

Table 5-2 Example of values of the conversion factors for the inputs for each paradigm

Input name	Unit	CExC	TEC	CEENE	EEA
E_FUEL	kgoe_{ex}/kgoe	1,023	1,060	1,088	1,023
M_ORE	kgoe_{ex}/kg	4,681	4,048	0,377	4,681

As showed in the schemes (Figure 5.1, Figure 5.2, Figure 5.3), only the exogenous inputs have been considered, taking into account that for each paradigm the set of inputs was different.

5.1.4.1 Cumulative Exergy Consumption (CExC) application

For the CExC paradigm application the energetic and material flows have been taken into account.
In the construction phase the overall inputs were: E_{FUEL}, M_{FUEL}, M_{EPS}, M_{ORE}.
In the operation phase the overall inputs were: E_{FUEL}, M_{FUEL}, M_{EPS}.

5.1.4.2 Thermo Ecological Cost (TEC) application

For the TEC paradigm application the energetic and material flows have been taken into account, keeping in mind that only non-renewable resources had to be considered.
In the construction phase the overall inputs were: E_{FUEL}, M_{FUEL}, M_{EPS}, M_{ORE}.
In the operation phase the overall inputs were: E_{FUEL}, M_{FUEL}, M_{EPS}.

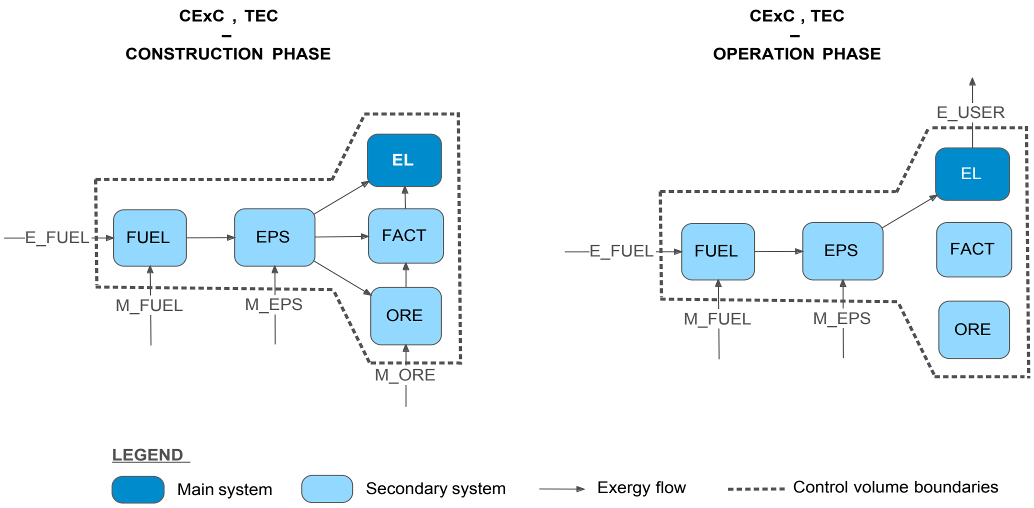


Figure 5.1 Schematic view of the model with CExC's impact categories flows for each phase of the cable life cycle

5.1.4.3 Cumulative Exergy Extraction from Natural Environment (CEENE) application

For the CEENE paradigm application the accounted flows were: energy, materials and land occupation.

In the construction phase the overall inputs were: E_{FUEL}, M_{FUEL}, L_{FUEL}, M_{EPS}, L_{EPS}, L_{FACT}, M_{ORE}, L_{ORE}, L_{EL}.

In the operation phase the overall inputs were: E_{FUEL}, M_{FUEL}, L_{FUEL}, M_{EPS}, L_{EPS}, L_{EL}.

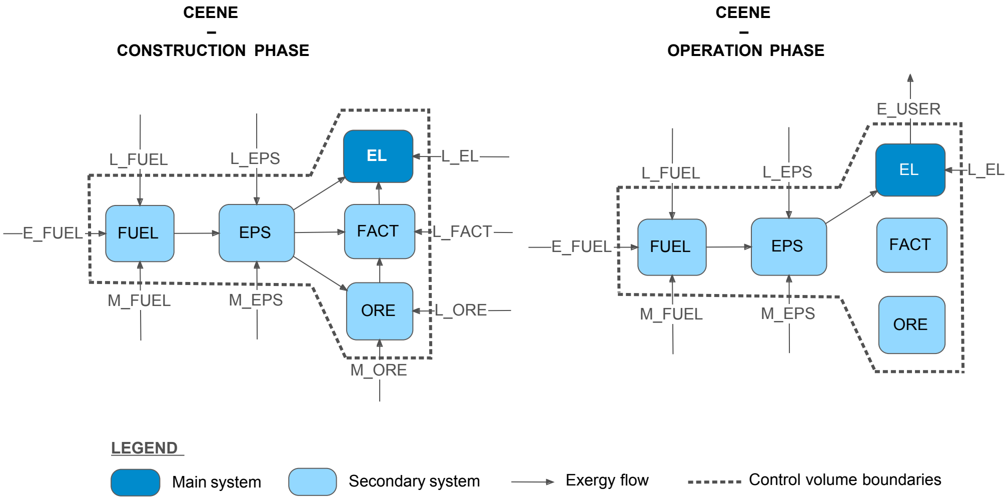


Figure 5.2 Schematic view of the model with CEENE's impact categories flows for each phase of the cable life cycle

5.1.4.4 Extended Exergy Assessment (EEA) application

For the EEA paradigm application the accounted flows were: energy, materials, labor and capital. Emission abatement costs were neglected, since non-present in the model.

In the construction phase the overall inputs were: E_{FUEL}, M_{FUEL}, H_{FUEL}, K_{FUEL}, M_{EPS}, H_{EPS}, K_{EPS}, H_{FACT}, K_{FACT}, M_{ORE}, H_{ORE}, K_{ORE}, H_{EL}, K_{EL}.

In the operation phase the overall inputs were: E_{FUEL}, M_{FUEL}, H_{FUEL}, K_{FUEL}, M_{EPS}, H_{EPS}, K_{EPS}, H_{EL}, K_{EL}.

Finally, the exergetic cost of decommissioning has been added, considering it numerically equal to the exergetic cost of the construction.

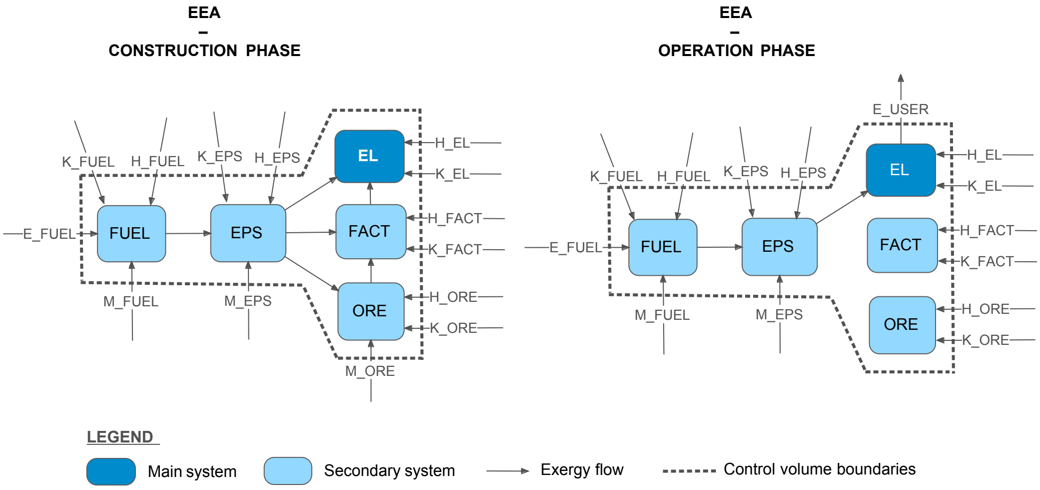


Figure 5.3 Schematic view of the model with EEA's impact categories flows for each phase of the cable life cycle

5.1.5 Results

As announced at the beginning of this chapter, the diameter size of the wire has been varied both to find the optimal value, which minimize the system's exergetic cost, and so its resource consumption, and to analyse the trend of the exergy cost of the system, over its life cycle, with the variation of the diameter.

The optimal values found for the diameter that minimize the consumption of resources are showed both in the graphs (Figure 5.4, Figure 5.5) and in the Table 5-3.

Table 5-3 Values of optimal size of cable diameter and relative resources consumption varying the paradigm applied

Method	*Diameter [mm]*	*Resources [kgoe$_{ex}$]*
CExC	3,67	32,63
TEC	3,78	31,87
CEENE	4,70	22,09
EEA	3,05	53,15

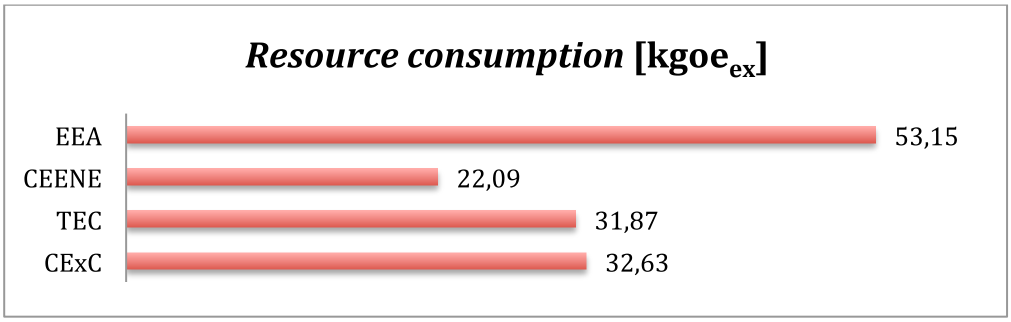


Figure 5.4 Resources consumption corresponding to method applying the optimal size of cable diameter found

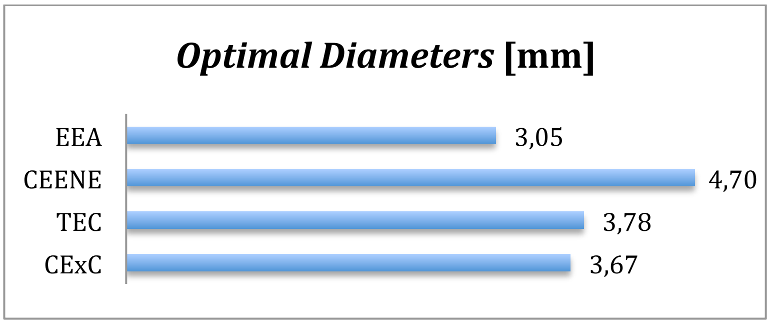


Figure 5.5 Values of optimal diameter size, which minimize resource consumption chosen a paradigm

The results remark the fact that taking into consideration one paradigm, out of four, will let to a configuration that may not be found when applying another paradigm.

On the side of resource consumption results are also different. In case of the CEENE, resource consumption is the minimum, while EEA is the paradigm that let register the higher value of consumption.

The EEA value of resource consumption results higher than the other paradigms because, except for land use in CEENE, there are the same factors of the other paradigms, but with the addition of monetary capital and labor, which seem to make a big difference in the absolute terms (Figure 5.4).

The CEENE, on the other side, have a conversion factor of the metal ore input that is lower than the others, which may probably end up being the most influent parameter in the computation of resource consumption, compared with the other methods.

TEC and CExC values of resource consumption are in the middle. But, The value of TEC resource consumption is higher than the CExC one, mainly because, even if they have the same inputs and no renewable resources are introduced in the main system or in the secondary systems, the numeric value of the conversion factor of the metal ore input is higher for the paradigm of CExC.

The graph of Figure 5.6 shows how much different paradigms give quite different results, since the curves, representing the life cycle exergy cost of the wire varying its diameter size, are not coincident, although having similar shape.

The CExC curve is slightly higher than the TEC curve because in this example they do have the same inputs, but the value of the copper input is smaller in TEC case ($M\_ORE_{TEC}=4{,}048<M\_ORE_{CExC}=4{,}681$), and for this reason, with the increase of the diameter size, the weight of the metal withdrawn is higher for CExC. The CEENE curve is lower than the other curves mainly because the exergy cost of the copper is significantly lower than the other paradigms (see Table 5-2).

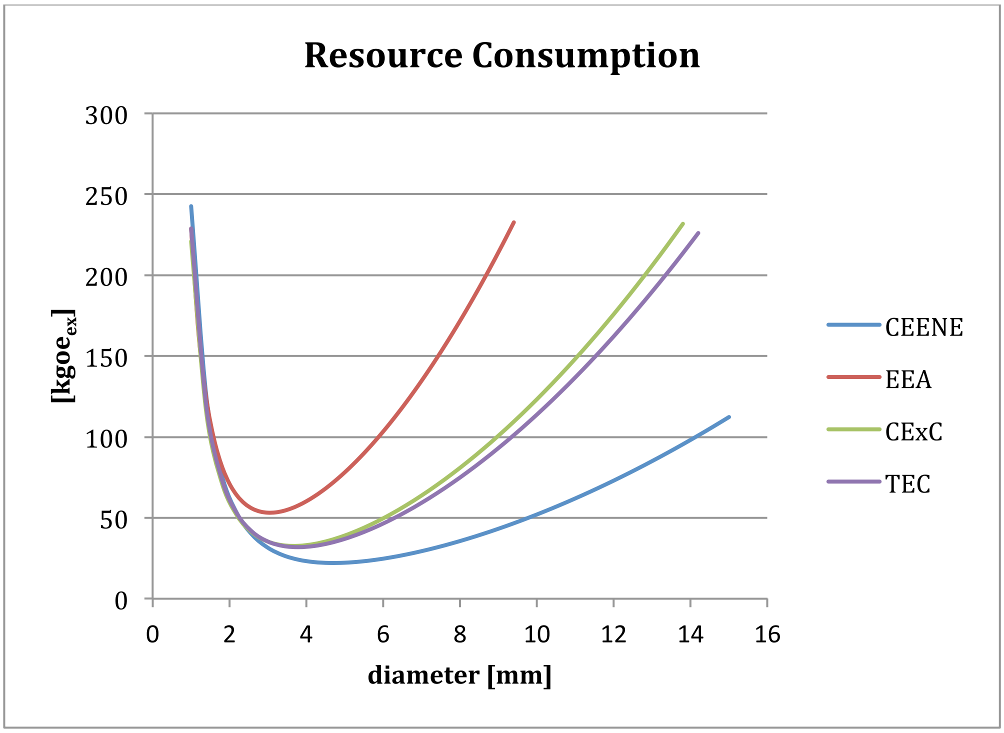


Figure 5.6 Comparison of resources consumption for different methods in respect to diameter values

Final remarks

Importance of natural resources

In today's society, natural assets are one of the main basis to create all goods and services, which are traded, used and consumed.

Energetic resources are fundamental for the sustainability of our consumption of both material and energetic commodities; therefore countries are, generally, energy dependent more than money dependent. For these reasons energy resources need more attention then other natural resources, and fair assessments with a life cycle approach should be principally focused on their consumption.

Depletion

It has been stressed how much natural resource depletion is a crucial issue for the sustainability of our society and that a proper assessment could help in finding the right path to avoid, or at least diminishing, this phenomenon.

The problem of depletion is linked mainly with the concept of scarcity, which has not jet been unanimously defined in the field of exergy analysis. Consequent to that, exergy-based methods could be part of the solution of the natural resource depletion problem.

Exergy

Among the cited numeraires exergy seems to be the best fit, when talking about natural resource consumption and, mainly, when the energetic ones have to be considered.

Exergy cannot be used as a criterion for depletion of natural resources, because, even if it measures the availability, it does not include scarcity in its definition, so only consumption or inefficient use of natural resources can be measured. [108]

Even if not everyone agrees with that, it seems that the concept of exergy is more intuitive in comparison with the concept of entropy. Moreover, when analysts of different fields meet and join together their competencies, they should be able to understand each other easily avoiding incomprehension.

Exergy is also regarded as a 'key component' for achieving sustainable development. [26]

Thermoeconomics

Thermoeconomics appears to be the perfect link between thermodynamics and economics. The thermoeconomic approach turns out being a valid way to calculate the optimal working point of a system and to locate losses within system components. In addition, it also applies to both engineering and economic evaluations.

Another problem has emerged in the terminology used, first, among the paradigms, and, second, between the economic and the process engineering fields. Thermoeconomics seems to be going in the direction of unifying the terminology starting from the roots, introducing the word 'cost' aside of the word 'exergy'. Another word always confusing and that should be clarified is 'value', because the 'value of something' represents, for an engineer, the physical content of that something, for an economist is a measure of the benefit that an economic actor can gain from either a good or service [117].

A convergence at least on the terminology needs to be found to pursue a sustainable development, which is always more multidisciplinary, needing an always more interdisciplinary approach.

Process analysis

When very detailed data are available, process analysis can be a good approach. Probably, in order to be sure of not making big mistakes one should look at the upstream processes of the inputs of the analysed system and be sure that their modelling can be performed easily. Otherwise the input-output analysis or hybrid approaches must be undertaken.

Remembering I-O analysis has the risk of obtaining not up to date results, due to database obsolescence.

Paradigms: theoretical problems

Among the reviewed paradigms no big relevance seems to have ecological processes, which in some cases can represent a bottleneck in the use of natural resources (e.g. biomass). Emergy is a proposed numeraire, someone in fact is trying to merge the cumulative exergy cost with the concept of emergy but the applicability of this method is still under analysis. [115]

Also ecological economics and industrial ecology should be explored and studied to fill the gap between the industrial and the ecological world.

Mastery in ecological fields is required to well address this problem, since the industrial sector, as it is, does not care so much about how its inputs are created or absorbed.

A unique framework is needed to allow validation and comparison of results. One suggestion is to try in build one paradigm that can comprehend all the others.

Paradigms: applicative problems, linked to the case study

All the methods analysed in this work can result valid and solid at first, but after their comparison with a simple example some discrepancies appears, and two of them are visible:

1. the optimal working points, in our case the optimal diameter size, do not result the same;
2. the resources consumed, measured with exergy destruction, are also different.

These two points clearly show the necessity of clarification and of a meeting point for those paradigms using exergy as numeraire. Further in-depth analysis are surely necessary, to understand which one of the existing paradigms is the best fit for resource consumption assessment.

The results of exergy-based analysis should also be compared with economic analysis, but if the first lack of consistency among the paradigm to use, the confrontation with another field, probably, would also lack of consistency.

Appendix A

Minimum separation work (MSW) theory

Since mixing processes are highly irreversible and the process of separation needs effort to be pursued, when an industrial process generate more than one useful product the minimum separation work (MSW) theory can be used to allocate the proper exergy cost to each of the products [118].

The isothermal MSW is defined as “the minimum work required by separating a homogeneous mixture into each pure component at constant temperature and pressure” [119]. In formula [118]:

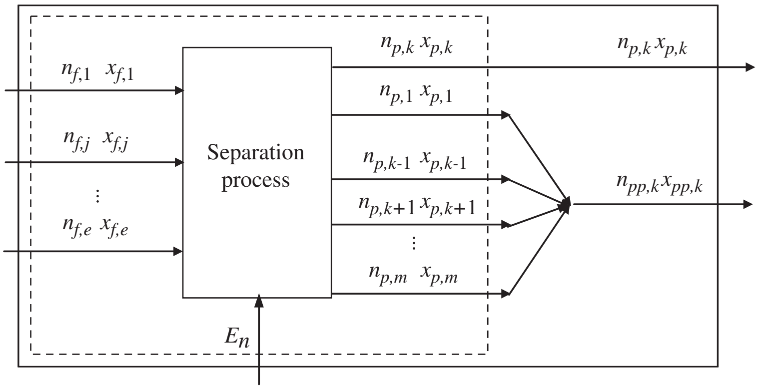
$$MSW = -RT\sum_{i=1}^{c} x_i \ln(\gamma_i x_i) \tag{5.3}$$

where:

- MSW is the MSW required by separating 1 kmol of mixture into pure component (kJ/kmol)
- R is the universal gas constant (kJ/kmol K)
- T is the constant temperature (K)
- x_i is the mole fraction of component i in the mixture
- γ_i is the activity coefficient of component i in the mixture, and
- c is the total number of components in the mixture.

For a mixture with a flow rate n (in kmol/s) the minimum separation power of mixture (MSPM) in kW results:

$$MSPM = n\ MSW \tag{5.4}$$



A separation process flow diagram [118]

For a separation process, like in the figure above, the minimum separation power of a separation process (MSPS) is:

$$MSPS = \sum_{j=1}^{e} MSPM_{f,j} - \sum_{k=1}^{m} MSPM_{p,k} \tag{5.5}$$

And the minimum separation power of product (MSPP) of the *k*th stream is defined as “the minimum separation power consumed in the fictitious separation process” [118], and it is expressed by

$$MSPP_k = \sum_{j=1}^{e} MSPM_{f,j} - MSPM_{p,k} - MSPM_{pp,k} \tag{5.6}$$

The MSPP, then, can be used as an allocation parameter. For example, if there are three feed streams and four products, the exergy cost allocated to the *k*th product will be

$$C_k = \frac{MSPP_k}{\sum_{k=1}^{4} MSPP_k}\left(C_{tot,c} + C_{tot,o\&m}\right) \tag{5.7}$$

In (5.7) between parentheses there are the total costs of construction, and the total cost of operation.

Appendix B

Model Data sources (source – year)

ENEL – end of 2012

BUREAU OF LABOR STATISTICS of UNITED STATES – 2010

IEA DATA UNITED STATES – 2010

WORLD MINERAL PRODUCTION - BRITISH GEOLOGICAL SURVEY – 2010

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