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Exergy and Exergy Cost Analysis of production systems incorporating renewable energy sources

Settore scientifico-disciplinare: **Area 09**

DOTTORANDO / A

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Abstract

Exergy is a thermodynamic quantity capable of measuring the conversion of material and energy flows into comparable terms based on the capacity of such flows to generate mechanical work as a useful effect and identifying and quantifying the thermodynamic inefficiencies of a generic process by means of the exergy destruction term.

Because of its properties, exergy is a convenient tool for the calculation of the global resource consumption of both natural and engineering processes. Therefore, there are different exergy-based approaches. Every exergy-based approach has its advantages and its drawbacks. It even has its own spatial and temporal domain [1].

Exergy based account methodologies do not account for the ecological processes and products. This is something saviour if the sustainability is the aim and the goal. Indirect cost of resources consumption must be counted. The exergy cost of mineral resources which are not renewable is not their chemical exergy embodied in them only but also the cost of exergy that has been to be spent to reconcentrate these resources to be available for the upcoming generations [2]. As it is matter of sustainability, considering the indirect exergy cost is very important.

This Thesis presents a conceptual development of sustainability evaluation, through an exergy-based Indicator, by using the new concept of the Thermoeconomic Environment (TEE). The exergy-based accounting methods here considered as a background are the Extended Exergy Accounting (EEA), which can be used to quantify the exergy cost of externalities like labor, monetary inputs, and pollutants, and the Cumulative Exergy Consumption (CExC), which can be used to quantify the consumption of primary resources “embodied” in a final product or service.

Also, the new concept of bioresource stock replacement cost is presented, highlighting how the framework of the TEEC (Thermoeconomic environmental cost) offers an option for evaluating the exergy cost of products of biological systems. The sustainability indicator is defined based on the

exergy cost of all resources directly and indirectly consumed by the system, the equivalent exergy cost of all externalities implied in the production process and, the exergy cost of the final product.

The new proposed methodology within thesis, via the cumulative exergy consumption (CExC), calculates the exergy cost of photosynthesis and bio-energy production, as together they form the best available technology when it comes to closing the carbon cycle. This approach ties together the “cradle to grave” to the “grave to cradle”, standardises the TEEC (Thermoeconomic Environment Cost) calculations and enables comparisons between fuel and non-fuel mineral consumption. As an indicator to measure the sustainability of resource depletion, the TEEC states the physical and economic costs of making a fuel and non-fuel resource available to society, not just from a natural deposit, but from our waste streams and our Earth’s sinks (landfills, atmosphere, and polluted oceans), relative to a depleted Earth.

The case studies of this thesis show the calculation of the exergy consumed by Nature and society to produce 1 MJ of Bio-equivalent fuel to be stored as manmade replacement of the fossil fuel (Oil, Coal, and Natural Gas) which naturally produced by the ecosystem. The Exergy replacement cost of fuel will be calculated for the entire life cycle from solar radiation to fuel. “From Solar radiation to biomass” is the photosynthesis stage and “From Biomass to fuel” is the Bioproduction stage. After calculation of the exergy replacement cost of producing Bio-equivalent fuel, the exergy cost of producing electrical energy based on different technologies is calculated. Then, The Sustainability indicator is calculated based on the new proposed approach in comparison to other approaches that take ecological products and services in consideration.

In comparison to the world mineral depletion evaluated by Valero and Valero [90]. Using this new method, we found that using the HHV as a proxy caused, on average, a forty-fold sub-estimation of the physical cost of fossil fuel depletion when considering solar radiation to fuel. The new method also delivers a paradigm shift towards an TEEC approach emphasize on function instead of chemical composition. The idea of sustaining a chemical composition is not appropriate and is a superfluous barrier to the further development of the TEEC calculation and its role in forming environmental debates.

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Contents

Nomenclature

$\dot{W}$	Mechanical Work flow rate (Watt)
$\dot{Q}$	Heat Flow rate (watt)
$\dot{m}$	Mass flow rate (kg/s)
E	Exergy (J)
$\dot{E}_Q$	Exergy stream associated to Heat transfer (Watt)
$\dot{E}_w$	Exergy stream associated to Mechanical work
e	Specific exergy (J/kg)
$\dot{E}_{des}$	Exergy destruction stream (watt)
z	Elevation (m)
V	Velocity (m/s)
u	Specific internal energy (J/kg)
P	Pressure (bar)
v	Specific Volume (m^3/kg)
T	Temperature (Celsius Degree)
s	Specific entropy (J/kg.k)
MM	Molecular Mass (gm/mole)
μ	Chemical composition
X	Molar fraction
V'	Volume (m^3)
t	Time (sec)
$\Delta\dot{S}_{gen}$	Entropy generation (J/k)
η_{ex}	Exergetic efficiency
$\dot{C}_m$	Monetary Cost flow rate($/sec) associated with exergy stream
$\dot{Z}$	Investment Cost flow rate ($/sec)
c_m	Specific monetary cost flow rate($/J) associated with exergy stream
M	Emergy (sej)
τ	Transformity (sej/J)
B	Available Energy (J)
Z	Capital Investment ($)
C	Exergetic Cost (J)
η	Thermodynamic degree of perfection

Γ	Allocation Matrix
γ	Transaction coefficient matrix
I	Identity matrix
α	First econometric coefficient
f	Consumption amplification factor
N_h	population numerosity
Wh	Working hours (Hrs/year)
N_w	Number of workers
M_{Fin}	The monetary circulation due to financial activities ($)
Y	The gross cumulative wages ($/year)
y	Specific yearly wage per capita ($/worker year)
β	Second econometric coefficient
M2	Monetary aggregate ($/year)
EE	Extended exergy (J)
eec	Extended exergy cost (J/kg, J/J, J/unit)
ee_c	The exergy equivalent of capital (J/$)
δ	Natural growth rate of the bioresource in a reservoir
ε	Extraction rate of the bioresource from a reservoir
ρ	Fraction of the bioresource required for the replacement
κ	Growth rate in the extended system required for the replacement
C_{ex-P}	TEEC of the product P
C_{ex-RES}	TEEC of the product P, considering only RES
C_{ex-PRS}	TEEC of the product P, considering only Partially RES
C_{ex-NRS}	TEEC of the product P, considering only non-RES
C_{ex-BSR}	TEEC of the product P, considering only the exergy BSR cost of Partially RES
C_{ex-Bep}	TEEC of the product P, considering only the ERC of mineral non-RES
i_{ex-TEE}	Exergy-based resource sustainability indicator
$M^{'}$	Amount of bioresource in a reservoir
$M_0^{'}$	Bioresource stock at instant t=0
dR/dt	Flow of bioresource required for stock replacement

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1. Introduction

This chapter aims to clarify the theoretical background of the new proposed approach, highlight the limitations of the current literature when used in this context, and the objective and novelties of the thesis.

1.1. Exergy and exergy analysis

Exergy analysis is a thermodynamic analysis that contains both first and second law. Exergy analysis is a quantitative analysis to measure the energy degradation (the decrease of its capacity to generate useful work) in conversion process. The concept of useful work has been initially introduced by Gibbs and Maxwell as a function called available energy that expresses the capacity of a system to produce external work when proceedings from initial state to its stable equilibrium states through series of reversible processes [4,5]. The method of exergy analysis has been developed both in its fundamentals and in several applications in the seventies through the works of Gaggioli, Moran, Beyer, Szargut, and many others.

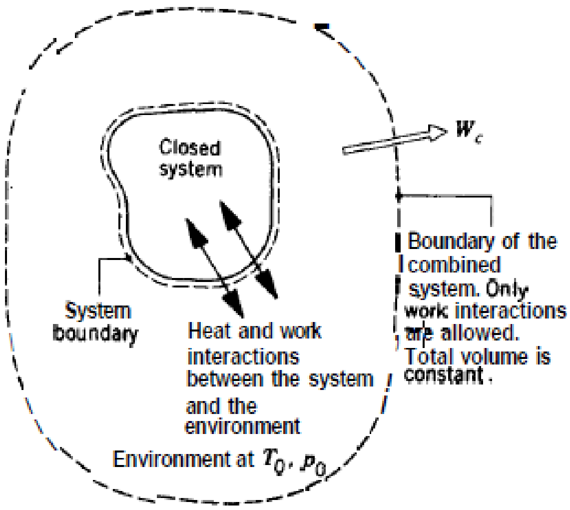

Figure 1 Combined system of closed system and environment. Adapted from [6].

With the reference to Fig. [1], Exergy can be defined as the amount of useful work that can be extracted from a system when it is brought to equilibrium with its reference environment through a series of reversible process in which the system can only interact with such environment [6]. The "exergy accounting" function for an open system has been analytically formulated by Bejan. It had been derived by applying energy and entropy balances to the system shown in Fig. [2].

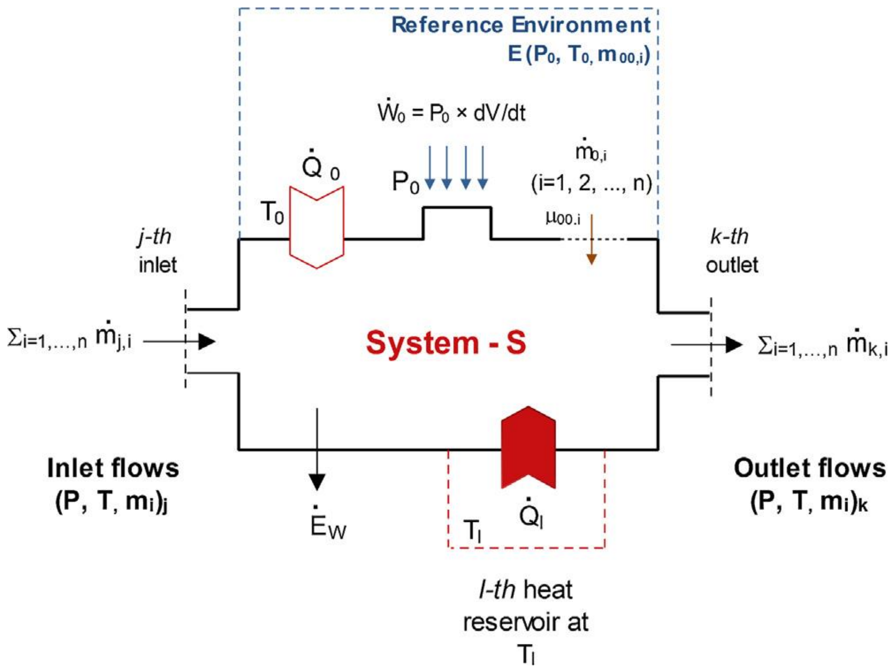

Figure 2 Control volume for exergy balance. Adapted from [7]

As Shown in Fig. [2], System can interact with only the reference environment in the form of exchanging work ($\dot{W}$), heat ($\dot{Q}$) and mass ($\dot{m}$) and with heat R_ha source R_i and an outlet reservoirR_r [6].

$$\frac{dE}{dt} = \sum_{i=1}^{p} \left(\dot{E}_Q\right)_i - \dot{E}_w + \sum_{j=1}^{q} (\dot{m} \cdot e_M)_j - \sum_{k=1}^{r} (\dot{m} \cdot e_M)_k - \dot{E}_{des} \qquad (1)$$

Since Exergy is not conserved, the word "balance" is not appropriate and the term "exergy accounting" has been adopted. The term $\dot{E}_{des}$ in Eq. (1) is a virtual term introduced with the purpose of balancing the exergy equation, but it does not correspond to any physical flux. Following the previous classification, the specific exergy of a stream of matter consisting of n components, e_M is defined as [7,8]:

$$e_M = g(z_1 - z_0) + \frac{1}{2}(V_1^2 - V_0^2) + (u_1 - u_0) + P_0(v_1 - v_0) \qquad (2)$$

$$-T_0(s_1 - s_0) + \frac{1}{MM_{mix}} \sum_{i=1}^{n} (\mu_{i,0} - \mu_{i,00}) X_i$$

Where $e_{pt} = g(z_1 - z_0)$, and $e_{kn} = \frac{1}{2}(V_1^2 - V_0^2)$ are the specific exergy components associated with potential and kinetic energy, respectively. By neglecting both these components, the specific energy of the stream can be defined as a function of two main components which are the physical exergy component and the chemical exergy component.

$$e_{ph} = (u_1 - u_0) + P_0(v'_1 - v'_0) - T_o(s_1 - s_0) \quad (3)$$

$$e_{ch} = \frac{1}{MM_{mix}} \sum_{i=1}^{n} (\mu_{i,0} - \mu_{i,00}) X_i \quad (4)$$

When the system is closed with respect to its reference environment and attains thermo-mechanical equilibrium with the reference environment, this equilibrium is called the Environmental State (subscript “0”), system temperature would be equal to T_0 and its pressure equal to P_0 .

At this point the system chemical composition may be different from the chemical composition of the reference environment. If the system is open allowing material exchange between the system and the reference environment, this material exchange may take place until the system reach another equilibrium state called Dead State (subscript “00”) where Temperature, Pressure, and chemical composition of the system is equal to these of the reference environment ($T = T_0 = T_{00}, P = P_0 = P_{00}, \mu_i = \mu_{i,00}$) .

Exergy can be transfer from the system to the surrounding while reaching the physical and chemical equilibrium with the reference environment. Exergy can also be transferred by doing work or transferring heat through the system boundary. The exergy associated with work $\dot{E}_w$ and heat transfer $\dot{E}_Q$ can be defined as following [6-8].

$$\dot{E}_w = \dot{W} - P_0 \frac{dV'}{dt} \tag{5}$$

$$\dot{E}_Q = \dot{Q}\,(1 - \frac{T_0}{T}) \tag{6}$$

In contrary to Energy as a thermodynamic quantity that cannot be generated or destructed, Exergy can be destructed. Exergy destruction $\dot{E}_{des}$ happens due to irreversibility sources within the system and hence entropy generation. Exergy destruction is equal to the reference temperature multiplied by the entropy generation as shown in the following formula [5].

$$\dot{E}_{des} = T_0 \cdot \Delta\dot{S}_{gen} \tag{7}$$

Traditional exergy analysis comprises in the application of the exergy balance (1) to a defined control volume, with the scope of tracing and calculating exergy destructions and efficiencies. The word System identifies all the possible objects susceptible of an energy analysis, ranging from simple stand-alone thermodynamic processes to more complex ones resulting from combinations of more processes and components. There is a consensus today among System Analysts that the rational use of resources must be assessed with the aid of both energy and entropy concepts, since the presence of irreversibility in a process increases the amount of primary resource needed to attain the same design objective [6-8].

A set of general guidelines for performing an exergy analysis of a system is the following [9]:

- Univocally define the system by properly selecting the control volume.
- Define an appropriate reference environment, specifying whether it is steady and uniform or not.
- Compute mass, energy, and entropy balances of the system during the process.
- Apply the exergy balance to the system.

A key outcome of such an analysis is the exergy efficiency of the process. For a clearer understanding of this concept, it is convenient to rewrite the exergy balance in Eq. [1] according to the Fuel-Product paradigm (F–P) as introduced by Tsatsaronis [6], and if the system of Fig. [2] operates at steady state, the exergy balance in Eq. [1] can be rewritten as follows:

$$\dot{E}_{Fuel} = \dot{E}_{Product} + \dot{E}_{Loss} + \dot{E}_{des} \tag{8}$$

$$\eta_{ex} = \frac{\dot{E}_{Product}}{\dot{E}_{Fuel}} = 1 - \frac{\dot{E}_{Loss} + \dot{E}_{des}}{\dot{E}_{Fuel}} \tag{9}$$

1.2. Exergy Replacement Cost to evaluate sustainability: critical review

The Exergy Replacement Cost (ERC) is an indicator that is used to ascertain the sustainability of non-renewable resource depletion. Specifically, it measures the amount of exergy society would have to spend if it were obliged to re-capture and re-concentrate dispersed minerals back into a manmade usable deposit. Due to an assumption regarding the non-substitutability of fossil fuels, the original method failed to properly account for them.

The new proposed methodology within thesis, via the cumulative exergy consumption (CExC), calculates the exergy replacement cost of photosynthesis and bio-energy production, as together they form the best available technology when it comes to closing the carbon cycle. This approach ties together the “cradle to grave” to the “grave to cradle”, standardises the TEEC calculations and enables comparisons between fuel and non-fuel mineral consumption.

As an indicator to measure the sustainability of resource depletion, the TEEC states the physical and economic costs of making a fuel and non-fuel resource available to society, not just from a natural deposit, but from our waste streams and our Earth’s sinks (landfills, atmosphere, and polluted oceans), relative to a depleted Earth Fig. [3].

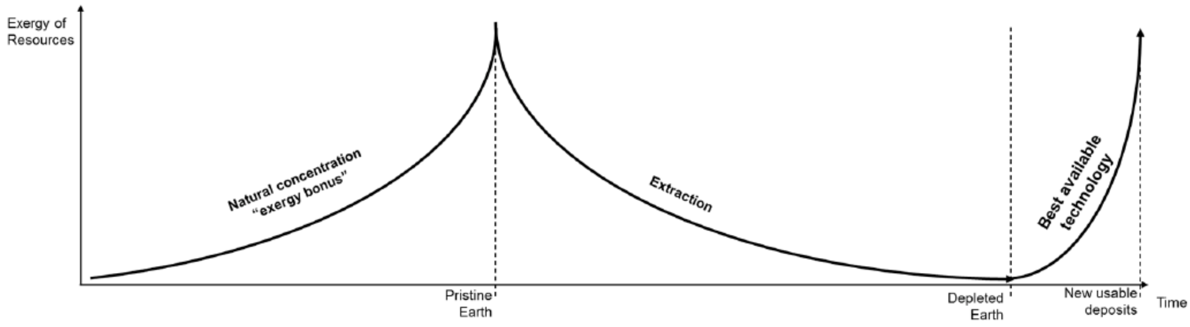

Figure 3 *Evolution of the exergy of Earth´s resources [83]*

Fig. [3], although theoretical, keeps true if society consumes faster than Nature can restore. The net effect of exhaustion will always follow a decline if consumption exceeds resource formation and concentration. The situation may change when society recognises that they are running out of inelastic goods, such as mineral (fuel and non-fuel). There is a considerable body of literature that applies the ERC to non-fuel mineral depletion. The ERC had not been applied previously to fuels.

The old methodologies tend to calculate their ERC using chemical exergy, through the high heating value which is not coherent with the new proposed methodology within this thesis. Chemical exergy is not the same as the exergy required to re-capture and re-concentrate carbon dioxide, using current best available technology, into a hydrocarbon that can be re-used. In fact, chemical exergy is the maximum amount of work that you can produce, in this case with a hydrocarbon. It is also equal to the minimum amount of work needed to produce it from reference state [91,92]. The difference between the ERC and chemical exergy is that the former denotes the cumulative exergy required to obtain a resource using current (or best) available technology, whereas the latter is the "minimum replacement cost". Moreover, the problem with Valero and Valero's [90] statement is that there is a fundamental assumption that the only way to create new fuel deposits is through geological processes that convert organic material into fossil fuels. And, although it is true that fossil fuels cannot be reproduced within an individual's lifetime with current best available technology, like carbon capture and storage, the carbon cycle can be closed through photosynthesis. Accordingly, best available technology, as it stands, is the planting and processing of fuel crops, or the diversion of organic wastes, to produce alternative fuels that accomplish the function of fossil fuels. In fact, since the publication of Valero and Valero [90], there has been increasing evidence to demonstrate that current technology from “crop to fuel” can, and has, partially replaced the functions of fossil fuels through biological equivalents, such as biofuels and biopolymers.

1.3. Thesis objectives

Through this thesis some of objectives are needed to be addressed which are.

1. Introducing of the new concept of Thermoeconomic reference environment: The TEE is defined as a set of reservoirs, where different kinds of natural resources are confined. All of them are surrounded by the zero-exergy matrix (the dead state). Each available resource has a specific exergy content greater than zero.
2. Presenting the Thermoeconomic Cost (TEEC) term which is the exergetic cost of a product as a sumption of exergy cost of all renewable, partially renewable, and non-renewable resources that have been depleted to produce the product. Not only these exergetic costs are included but also the exergetic cost of creating a bio-replacement of all Non-Renewable and partially renewable resources. So, it is a paradigm shift toward costing a natural resource not according to its intrinsic exergy but rather according to its function and its scarcity.
3. Revealing The Thermoeconomic Environment Cost Indicator ($i_{ex\text{-}TEE}$) as a One-dimensional Measure of Resource Sustainability.
4. Calculating the TEEC of fossil fuels including the exergetic cost of creating a bio-alternatives.

2. Exergy-based accounting approaches:

Various approaches can be found in literature using exergy as a basis for cost allocation, i.e. they look for a cost of goods and services in term of the exergy required at the boundaries of the system for obtaining the required production [10].

Exergy cost definition require (i) cost allocation rules and (ii) clear limits for the control volume, where the start of the exergy supply chains of the system is located and at which the unit exergy costs of all inputs are known. A concise review of exergy-based costing methods can be found in [11]. Some of Exergy-based accounting approach are critically reviewed within this chapter.

2.1. Thermoeconomic (exergoeconomic analysis)

The word "Thermoeconomic" was presented in 1961 by Tribus. More developments have been made by El-Sayed and Evans [13] in the US and by Elsner, Beyer, and others in Europe and in the eighteenth, Gaggioli extended the application of the theory. More recent, Tsatsaronis and Valero were able to produce a complete and elegant formalization of the method that is known now as Thermoeconomic cost theory or exergoeconomic [14-16]. Exergoeconomic analysis is a monetary costing technique that combines second law principles with traditional cost accounting methods.

Cost accounting in a company is concerned primarily with determining the actual cost of products or services, providing a rational basis for pricing goods or services, providing means for allocating and controlling expenditures, and providing information on which operation decisions may be based and evaluated. In conventional economic analysis. A cost balance is usually formulated for the overall system (subscript tot) operating at steady state [15].

$$\dot{C}_{m,P,tot} = \dot{C}_{m,F,tot} + \dot{Z}_{tot}^{CI} + \dot{Z}_{tot}^{OM} \tag{10}$$

The cost balance expresses that the cost rate associated with the product of the system ($\dot{C_{m,P}}$) equals the total rate of expenditures made to get the product which is the sum of the fuel cost rate ($\dot{C}_{m,F}$), the cost rate associated with capital investment ($\dot{Z}^{CI}$), and operating and maintenance ($\dot{Z}^{OM}$). The rates ($\dot{Z}^{CI}$) and ($\dot{Z}^{OM}$) are calculated by dividing the annual contribution of capital investment and the annual operating and maintenance costs, respectively, by the number of time units (usually hours or seconds) of system operation per year. The sum of these two variables is denoted by $\dot{Z}$.

$$Z = \dot{Z}^{\dot{C}I} + \dot{Z}^{OM} \quad (11)$$

For a system operating at steady state there may be several entering and exiting material streams as well as both heat and work interactions with the surroundings. Associated with these transfers of matter and energy are exergy transfers into and out of the system and exergy destructions caused by the irreversibilities within the system. Since exergy measures the true thermodynamic value of such effects, and costs should only be assigned to commodities of value, it is meaningful to use exergy as a basis for assigning costs in thermal systems [17]. Indeed, Thermoeconomics rests on the notion that exergy is the only rational basis for assigning costs to the interactions that a thermal system experiences with its surroundings and to the sources of inefficiencies within it. We refer to this approach as exergy costing. In exergy costing a cost is associated with each exergy stream. Thus, for entering and exiting streams of matter with associated rates of exergy transfer $\dot{E}_i$and $\dot{E}_o$ power $\dot{W}$, and the exergy transfer rate associated with heat transfer $\dot{E}_q$we write, respectively [18].

$$\dot{C}_{m,i} = c_{m,i}\dot{E}_i = c_{m,i}(\dot{m}_i \mathrm{e}_i) \quad (12)$$

$$\dot{C}_{m,o} = c_{m,o}\dot{E}_o = c_{m,o}(\dot{m}_o e_o) \quad (13)$$

$$C_{m,w} = c_{m,w}W \quad (14)$$

$$\dot{C}_{m,q} = c_{m,q}\dot{E}_q \quad (15)$$

Here $c_{m,i}$,$c_{m,o}$,$c_{m,w}$, and $c_{m,q}$denote average costs per unit of exergy in dollars per joule ($/J). Exergy costing involves cost balances usually formulated for each component separately. A cost balance applied to the kth system component shows that the sum of cost rates associated with all exiting exergy streams equals the sum of cost rates of all entering exergy streams plus the appropriate charges due to capital investment ($\dot{Z}_k^{CI}$) and operating and maintenance expenses ($\dot{Z}_k^{OM}$) [19]. The sum of the last two terms is denoted by ($\dot{Z}_k$). Accordingly, for a component receiving a heat transfer and generating power, we would write

$$\sum_o \dot{C}_{m,o,k} + \dot{C}_{m,w,k} = \dot{C}_{m,q,k} + \sum_i \dot{C}_{m,i,k} + \dot{Z}_k \tag{16}$$

This equation simply states that the total cost of the exiting exergy streams equals the total expenditure to obtain them: the cost of the entering exergy streams plus the capital and other costs. Note that when a component receives power (as in a compressor or a pump) the term $\dot{C}_{m,w,k}$ would move with its positive sign to the right side of this expression. The term $\dot{C}_{m,q,k}$would appear with its positive sign on the left side if there is a heat transfer from the component. Cost balances are generally written so that all terms are positive [20]. By introducing the cost rate expressions of Equation becomes

$$\sum_o (c_{m,o}\dot{E}_o)_k + c_{m,w,k}\dot{W}_k = c_{m,q,k}\dot{E}_{q,k} + \sum_i (c_{m,i}\dot{E}_i)_k + \dot{Z}_k \tag{17}$$

The exergy rates ($\dot{E}_o$, $\dot{W}$, $\dot{E}_q$,and$\dot{E}_i$) exiting and entering the kth component are calculated in an exergy analysis conducted at a previous stage. The term $\dot{Z}_k$is obtained by first calculating the capital investment and O&M costs associated with the kth component and then computing the levelized values of these costs per unit of time (year, hour, or second) of system operation [6].

The variables in previous Equation are the levelized costs per unit of exergy for the exergy streams associated with the kth component $c_{m,o}, c_{m,w}, c_{m,q}, c_{m,i}$.In analyzing a component; we may assume that the costs per exergy unit are known for all entering streams. These costs are known from the components they exit or, if a stream enters the overall system consisting of all components under consideration, from the purchase cost of this stream. Consequently, the unknown variables to be calculated from a cost balance for the kth component are the costs per exergy unit of the exiting material streams ($c_{m,o,k}$) and, if power or useful heat is generated in that component, the cost per unit of exergy associated with the transfer of power $(c_{m,w,k})$ or heat $(c_{m,q,k})$

2.2. Emergy analysis

Emergy analysis was developed by H.T. Odum as a part of larger theory about the functioning of ecological and other systems. In this theory, Odum explained how systems survive and organize in hierarchies by using energy efficiently in the way that generate the max power [33]. Emergy approach is probably developed in fifties when H.T. Odum identified the importance of energetics to ecology [31].

Emergy approach is a very interesting approach where all resources consumed to get a final product are presented in one thermodynamic quantity which is the emergy or “embodied energy”. Emergy analysis represents products and services in equivalents of solar energy. This approach accounts how much solar energy would be consumed to get a final product if solar energy is only the available resource. Emergy M is measured in solar embodied joules sej [30]. Emergy analysis considers the earth as a closed system with only three main energy resources which are the solar energy, tidal energy, and deep earth heat. All living systems sustain on another by contributing to an energy flow network where the low-grade energy is being converted into high grade energy and a degraded heat energy. All other kinds of energy that flow through earth can be derived from the three main energy resources. All these energies are scaled to solar equivalent to get a common unit. To get the solar equivalent of an energy needed for getting a specific product or services, the energy is multiplied by its solar Transformity. Solar Transformity (τ), is the solar energy required to get one joule of service or product [30]. It is measured in sej/J. The solar transformity of a product is its solar emergy (M) divided by its available energy (B), that is,

$$M = \tau B \tag{18}$$

Odum argues that the “energy flows of the universe are oragnized in an energy transformation hierarch” and that “the position in the energy hierarchy is measued with transformitites”. Therefore, transformity is regarded as a measure of energy quality. Most case studies rely on the transformities calculated by odum and co-workers to calculate the emergy of their inputs. Most transformities are calculated from the yearly emergy flow to the earth [31].

The emergy of economic inputs measured in terms of money is determined by multiplying the input in monetary units by the ratio of the nation´s total emergy to its economic gross national product.

$$M = Z\left(\frac{M_{nation}}{Z_{nation}}\right) \tag{19}$$

2.2.1. Emergy Algebra

Assigning emergy to each stream or node in a network requires an allocation technique as shown in Fig. [4]. Emergy is allocated to a stream according to the available energy of the outputs. When a stream is split without any energy transformation, transformity does not change its value and emergy is distributed for streams as shown in case (a).

In case (b) When there is energy transformation between streams. The emergy is not distributed but assigned entirely to each stream. This is based on the concept that they are co-products which means that none of the stream can be produced form the other independently. Assigning the emergy entirely to each stream adds complexity to the algebra and extra attention is required to avoid double counting when the emergy is combined.

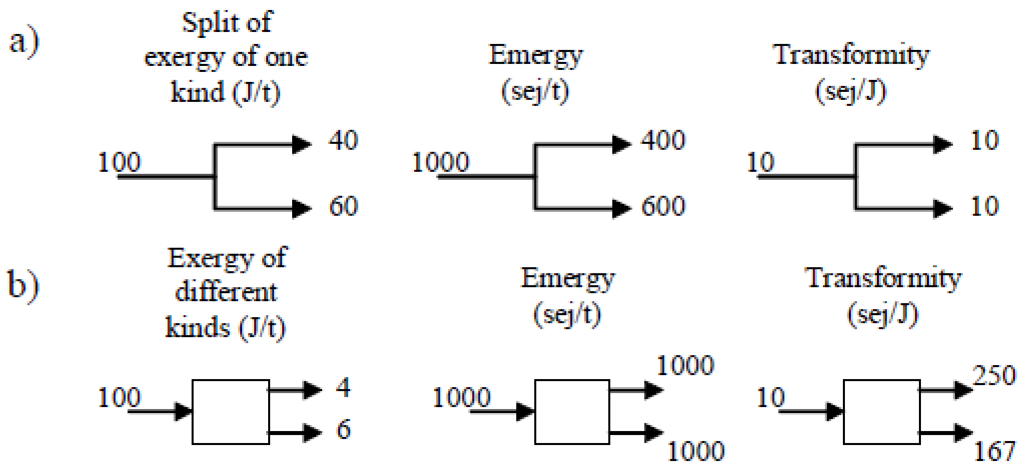

Figure 4 Emergy flow through network branches [30].

Fig. [5] shows how emergy is allocated to stream intersections [30]. Emergy is added when available energy of the same kind is combined, and when available energy of different kinds and sources are combined. However, when available energy of different kinds but same sources are combined, then the higher value of emergy is assigned.

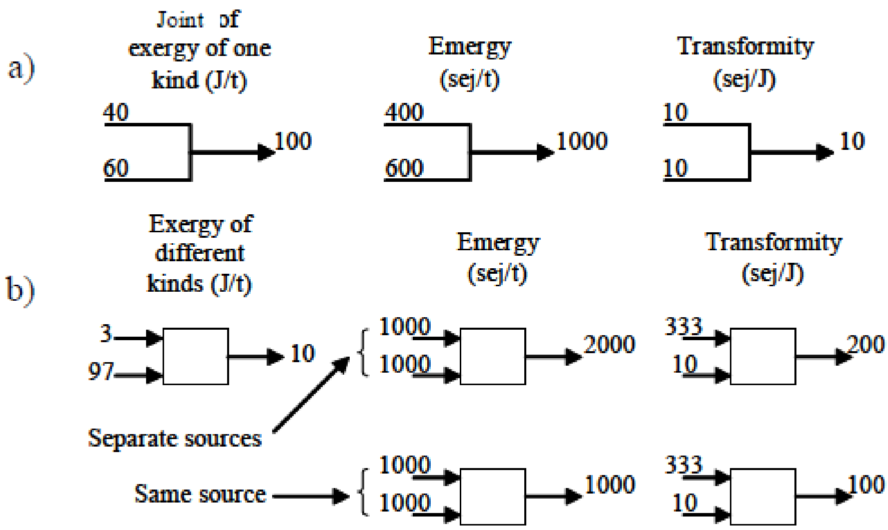

Figure 5 *Emergy flow with network joints [30].*

When a stream intersects with a feedback loop, emergy of loops are not accounted for in calculations to avoid double counting as shown in Fig. [6] [34].

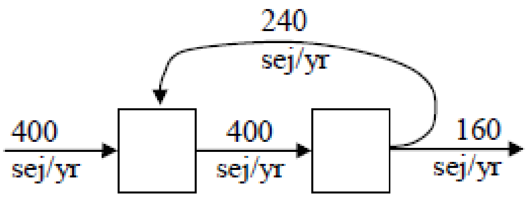

Figure 6 *Emergy flow with feedback*

2.2.2. Emergy Analysis of the main Earth Processes

This section is adapted from Odum´s book and recent Emergy folios [31, 32]. Fig. [7] shows the total emergy input to the Earth, often called global emergy budget, is the sum of the emergy of solar insolation, crustal heat, and tidal energy. Since they are independent, they are added. Other energy sources are assumed to be generated from these three sources, e.g., hemisphere general circulation, ocean circulation, global sedimentary cycle, etc. Most of them are considered co-products and therefore, their emergy equals the global emergy budget.

Solar insolation is the solar energy that reaches the Earth by radiation. Its available energy B_{si} has been calculated by multiplying the solar constant (4.4*10^{10} J/m^2-yr), the fraction of solar irradiation absorbed by the Earth (70 %) and the Earth cross section facing the Sun (1.27*10^{14} m^2).

$$B_{si} = (4.4 * 10^{10}) * 0.7 * (1.27 * 10^{14}) = 3.93 * 10^{24}\, J/yr$$

The transformity of solar insolation τ_{si} is unity, so emergy of solar insolation is $3.93 * 10^{24}\, J/yr$.

The energy of crustal heat has been calculated by adding the total heat released by crustal radioactivity (1.98*10^{20} J/yr) and heat flowing up from mantle (4.74*10^{20} J/yr). So, the available energy of crustal heat is 6.72*10^{20} J/yr. The total heat outflow from the surface is 13.21*10^{20} J/yr. The additional contribution of total heat outflow (6.49*10^{20} J/yr) is contributed from the above sources,

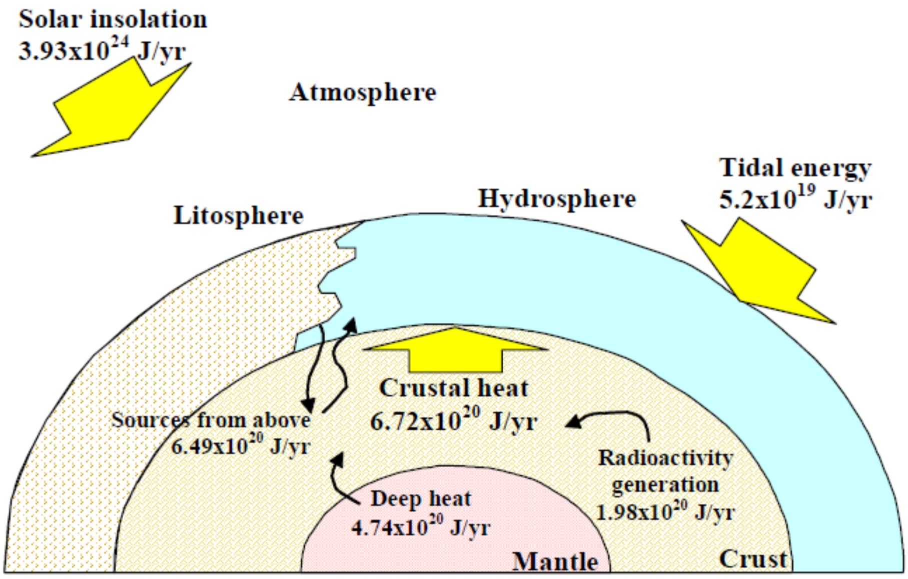

Figure 7 *Main energy flow on Earth. Adapted from [31].*

solar insolation, and tidal energy, by passing energy downward as compression and chemical potentials. The hear transfers from the above downward has the same quality of the heat generated from radioactivity and the deep heat; so, they all have the same transformity τ_{ch}. From Fig. [7], The emergy balance equation is

$$(3.93 * 10^{24}\, J/yr)\left(1\frac{sej}{J}\right) + \left(5.2 * 10^{19}\frac{J}{yr}\right)\tau_{te} = \left(6.49 * 10^{20}\frac{J}{yr}\right)\tau_{ch} \tag{20}$$

Where τ_{te} , τ_{ch} are the transformities of tidal energy and crustal heat, respectively. The solar insolation, crustal heat, and tidal energy contribute to generate an oceanic geopotential energy of $(2.14 * 10^{20}\ J/yr)$. The ocean geopotential energy has the same quality as the tidal energy; therefore, they have the same transformity. An emergy balance equation gives

$$(3.93 * 10^{24}\, J/yr)\left(1\frac{sej}{J}\right) + \left(6.72 * 10^{20}\frac{J}{yr}\right)\tau_{ch} + \left(5.2 * 10^{19}\frac{J}{yr}\right)\tau_{te} = \left(2.14 * 10^{20}\frac{J}{yr}\right)\tau_{te} \tag{21}$$

By solving Eq. [20] and [21], τ_{ch} and τ_{te} are obtained and equal to 11891 sej/J and 73923 sej/J respectively.

Emergy of crustal heat and tidal energy are equal to:

$$M_{ch} = (6.72 * 10^{20}) * (11891) = 8.06 * 10^{24} \frac{sej}{yr}$$

$$M_{te} = \left(5.2 * 10^{19} \frac{J}{yr}\right) * (73923) = 3.83 * 10^{24}\ sej/yr$$

Table 1 *Global emergy budget of the Earth*

	Available energy (J/yr)	Transformity (sej/J)	Emergy (sej/yr)
Solar insolation	$3.93 * 10^{24}$	1	$3.93 * 10^{24}$
Crustal heat	$6.72 * 10^{20}$	11981	$8.06 * 10^{24}$
Tidal energy	$0.52 * 10^{20}$	73923	$3.83 * 10^{24}$
Global budget			$15.83 * 10^{24}$

Odum and co-workers have determined the emergy of the main ecological process such Earth sedimentary cycle, the total surface wind, rainwater in streams, and waves absorbed on shore. Odum argues that the emergy assigned to each ecological process would be equal to the global emergy budget as they are considered as co-products of the global geological cycle and cannot be produced independently with less amount of the total emergy.

For instant, Odum calculated the emergy of the Earth sedimentary cycle by calculating the emergy per gram of sediment by estimating that a layer of approximately one inch (2.4 cm) of thickness of soil is removed from the continental land (area = $1.5*10^{18}$ cm^2) by erosion and replaced by earth uplift in a period of thousand years. The sediments´ flux is calculated by taking the product of the annual replaced layer and the average density of rocks (2.6 g/cm^3). So, the emergy per gram of sediment is the global emergy budget divided by the flux of sediments. The allocation of emergy would be based on the mass of sediments.

$$The\ flux\ of\ sediments\ = \frac{(2.4\ cm) * \left(2.6\frac{g}{cm^2}\right) * (1.5 * 10^{18})}{1000\ yr}\ =\ 9.36 * 1015\ g/yr$$

The emergy per gram of sediment is the global emergy budget divided by the flux of sediments

$$= \frac{15.83 *\ 10^{24}\ sej/yr}{9.36 *\ 10^{15}\ g/yr} = 1.69 * 10^9\ sej/g$$

To determine the emergy of non-renewable resources such as fossil fuel, solar input over geological time scales shall be accounted. This can be a problem because it is difficult to know the inputs and process over such a long time. So Emergy approach is not the approach to be taken for non-renewable fuels.

For example, Coal is a material in the earth crust but becomes accessible by human through the earth sedimentary Cycle. Then the emergy of coal may be approximated based on the earth sedimentary cycle. The Gibbs free energy of coal is 29302 J/g. Then the transformity of coal is,

$$\tau_{coal} = \frac{the\ emergy\ per\ gram\ of\ sediment}{Coal\ Gibbs\ free\ energy} = \frac{1.69 * 10^9 sej/g}{29302\, J/g} = 5.76 * 10^4 sej/J$$

To calculate other fuels transformity, an equivalence factor between fuels is used. Considering that the work generated from 1.65 J of coal is equivalent to that generated from 1 J of liquid motor fuel, the transformity of liquid motor fuel can be calculated as

$$\tau_{Motor\ fuel} = \left\{5.76 * 10^4 \frac{sej}{J_{coal}}\right\} * 1.65 \frac{J_{coal}}{J_{motor_{fuel}}} = 9.5 * 10^4 \frac{sej}{J_{motor_{fuel}}}$$

Considering that 81% of crude oil is used as liquid motor fuel and the remaining 19% is used as refining and transport, the transformity of crude oil can be calculated as

$$\tau_{crude\ oil} = \left\{9.5 * 10^4 \frac{sej}{J_{motor\ fuel}}\right\} * 0.81 \frac{J_{motor\ fuel}}{J_{crude\ oil}} = 7.7 * 10^4 \frac{sej}{J_{crude\ oil}}$$

The transformity of natural gas can be calculated by considering the natural gas is 20% more efficient in boiler than coal.

$$\tau_{natural\ gas} = \left\{5.76 * 10^4 \frac{sej}{J_{coal}}\right\} * 1.2 \frac{J_{coal}}{J_{natural\ gas}} = 6.9 * 10^4 \frac{sej}{J_{crude\ oil}}$$

2.3. Cumulative Exergy Consumption

An accounting method based on exergy only has been introduced by Szargut in 1973 [36]. This accounting method called “Cumulative Exergy Consumption” (CE_xC). Its aim is to compute the cumulative consumption of natural resources in term of exergy to produce a product and assign the “total natural resource cost” to the product. The preliminary formulation of CE_xC did not include the accounting of externalities ´exergy. Later, the theory has been adjusted to include the ecological cost which is calculated on a remediation basis [37].

Recently, the CE_xC and Exergy Costing theory were merged into a formally complete costing model to account for the natural resource’s consumption, leaving out though all monetary costs (capital, labour, and the monetary segment of environmental costs). It is remarkable that embodied exergy model is not an utterly new concept: already in the ‘70es, Costanza, Herendeen and Berry [39,40] had formulated a theory of “embodied energy”, in which the “cost” of a product was attained as a space and time integral of all the energy fluxes that create the “fuels” of the production process. However, Embodied Energy theory is based on the First Law of thermodynamic, it cannot account for the intrinsic thermodynamic difference between chemical, thermal and mechanical energy inputs, or outputs.

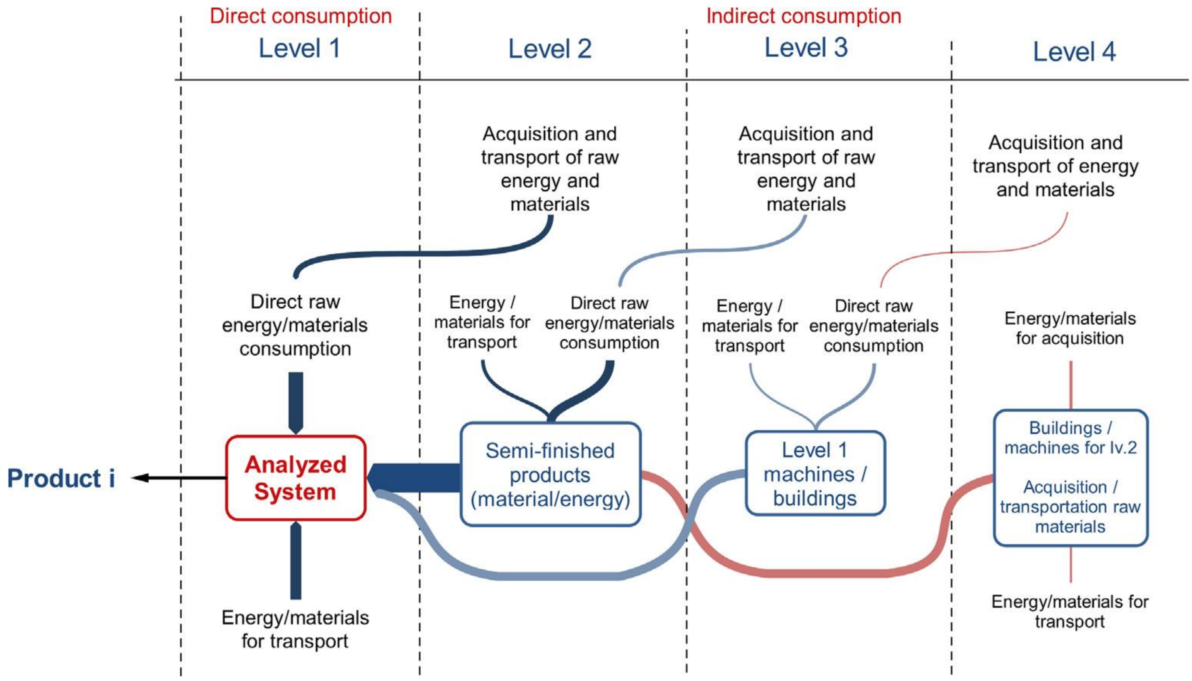

Figure 8 *Process method for CExC Calculations*

Fig. [8] reveals a crucial difference between direct and indirect exergy consumption Direct exergy consumption is represented by “level 1” processes: this is the amount of primary exergy directly utilized in the production of the product. For instance, direct exergy consumption in the electricity production from coal is the amount of coal and auxiliary exergy necessary to produce one Joule of electricity.

Indirect exergy consumption is represented by all upstream levels and is the amount of primary exergy spent to produce each one of the material and energy inputs to the system. Taking again the example of electricity production from coal, indirect contributions are the primary exergy needed to produce and transport coal; build, operate and decommission machines, buildings, trucks, etc.

The CE_xC values of the same flux may presume different values depending on the chain production of origin. For instance, two streams of superheated steam at the same pressure and temperature, one created by a gas-fuelled steam generator and the other by a heat recovery boiler, have two different CE_xC values. Lists of CE_xC values for many finished materials and energy vectors are available in literature [36,37].

2.3.1. Industrial Cumulative Exergy Consumption

Industrial Cumulative Exergy Consumption (ICEC) is an expansion of exergy analysis. It accounts for the exergy of all the natural resources used directly or indirectly to make a product [36]. Fig. [9] illustrate an ICEC analysis. A stream is a natural resource if it is a direct product from ecological processes and a raw material for human activities, for instance, coal, iron, and water stream. Industrial Cumulative Exergy Consumption (ICEC) of a process is the sum of the exergy of all the natural resources utilized in all steps of the process and previous processes in the production chain. In general, ICEC of the production chain C_p is

$$C_p = C_n = \sum_{K=1}^{N_i} C_{n,k} \tag{22}$$

where, N_i denotes the number of process units contained in the industrial production chain. $C_{n,k}$ and $C_{p,k}$ are the cumulative exergy of the natural resource entering and of the product existing the k-th process unit respectively. Exergy and cumulative exergy of natural resource inputs are considered to be equal in ICEC analysis, that is

$$C_{n,k} = B_{n,k} \tag{23}$$

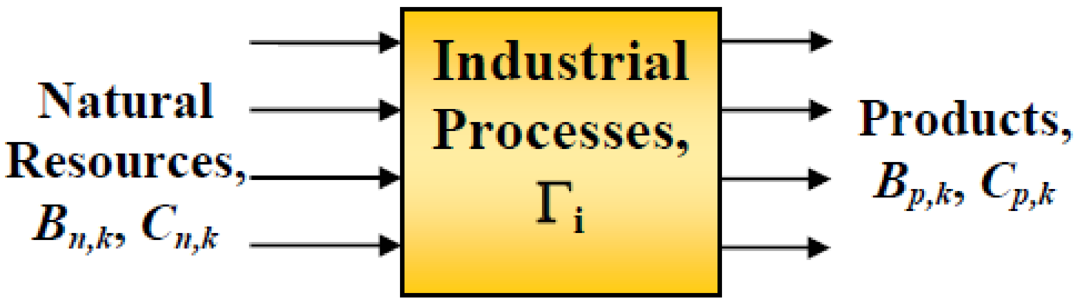

***Figure 9** Industrial Cumulative Exergy Consumption analysis.*

Industrial Cumulative Degree of Perfection (ICDP), ɳ is the ratio of available energy (B) of the final product(s) to the ICEC of the product(s). This is

$$\eta_p = \frac{B_p}{C_p} \quad \eta_{p,k} = \frac{B_{p,k}}{C_p, k} \tag{24}$$

Where, B_p is the vector of product exergies, $B_{p,k}$, η_p is the $N_i \times N_i$ diagonal matrix with $\eta_{p,k}$ Forming the diagonal terms, and C_p is the vector of product CE_xC.

The relationship between CE_xC for each product, $C_{p,k}$ and CE_xC of the inputs, $C_{n,k}$ may be written as,

$$C_p = \Gamma_i \cdot C_n \tag{25}$$

Where, C_n is the vector of input CE_xC, $C_{n,k}$, and Γ_i is the $N_i \times N_i$ allocation matrix.

2.3.2. Ecological Cumulative Consumption

Global exergy inputs are converted through ecological processes into ecological goods and services that are transformed into economic goods and services by industrial processes. Incorporating ecological processes in analysis requires extension of the system boundaries of ICEC analysis as shown in Fig. [10].

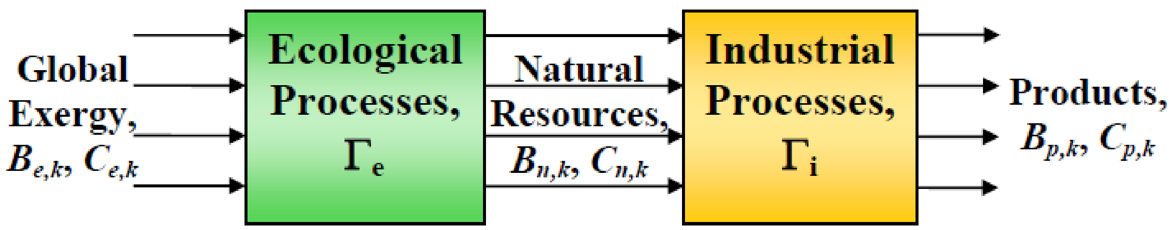

Figure 10 *Ecological Cumulative Exergy Consumption Analysis.*

The exergy and cumulative exergy of inputs that feed ecological processes are $B_{e,k}$ and $C_{e,k}$ respectively. exergy and CE_xC of natural resources, B_n and $C_n$respectively, can be connected through an equation

$$C_n = \eta_n^{-1} B_n \tag{26}$$

Where η_n is the $(N_i + N_e) \times (N_i + N_e)$ diagonal matrix with $\eta_{n,k}$ forming the diagonal terms. Ne denotes the number of units included in the ecological supply chain.

The exergy utilized in ecological processes to produce the natural resources and that for transforming natural resources to industrial products may be written as

$$C_n = \Gamma_e \cdot C_e \ \ and \ \ C_p = \Gamma_i \cdot C_n \tag{27}$$

Where Γe and Γi are the allocation matrices for representing ecological inputs to natural resource outputs and natural resources to industrial products, respectively. The cumulative exergy consumption in ecological and industrial processes (ECEC) to create each product may be written as

$$C_p = \Gamma \cdot C_e \tag{28}$$

Where Γ represents the overall allocation matrix for ecological and industrial processes together.

2.3.3. ECEC Computation

The previous equations for ECEC analysis do not provide sufficient details about how ECEC may be computed in practice. This section addresses such practical issues as allocation and network algebra.

Network Representation and Algebra

The network algebra of input-output analysis delivers a convenient and rigid way of analysing flow in any network. Any network may be represented as shown in Fig. [11] which show a generic system of three units interact together.

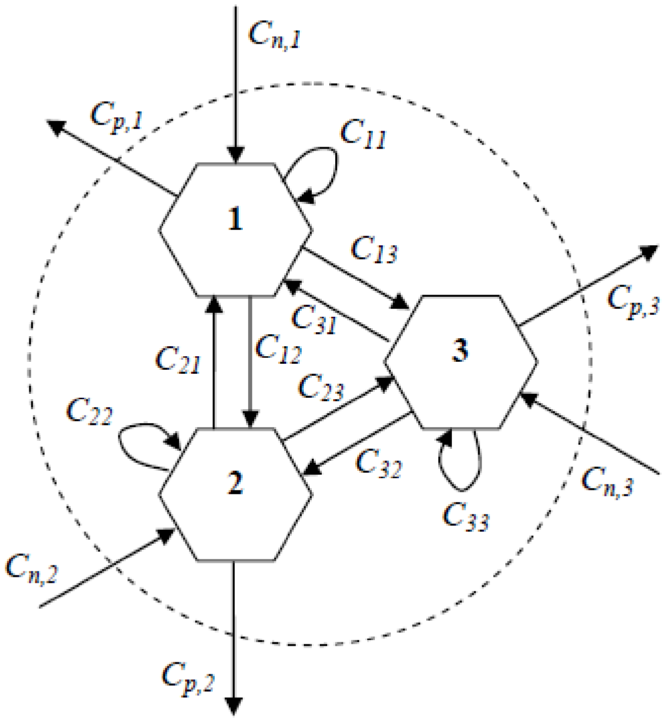

Figure 11 *Generic presentation of input and output analysis*

C_{ij} represents a direct transaction from the i-th to the j-th unit. Input-output analysis requires that the element being analysed is conserved, for example mass, energy, cumulative exergy, money, etc. Therefore, C_i is the sum of all the direct inputs to the i-th unit, which also equals the sum of all the outputs from the i-th unit. The transaction coefficient, γ_{ij}, represents the fraction of C_i that is transferred to the j-th unit. $\gamma_{p,i}$ (Transaction Coefficient) is the fraction of C_i leaving the system. Transaction coefficients carry information about the allocation method used. The interaction between the three units shown in Fig. [11] can be represented in tabular from for better understanding as shown in Table [2].

Table 2 *Tabular representation of Fig. [10].*

Units	1	2	3	Output	Total
1	$C_{11} = \gamma_{11}C_1$	$C_{12} = \gamma_{12}C_1$	$C_{13} = \gamma_{13}C_1$	$C_{p,1} = \gamma_{p,1}C_1$	C_1
2	$C_{21} = \gamma_{21}C_2$	$C_{22} = \gamma_{22}C_2$	$C_{23} = \gamma_{23}C_2$	$C_{p,2} = \gamma_{p,2}C_2$	C_2
3	$C_{31} = \gamma_{31}C_3$	$C_{32} = \gamma_{32}C_3$	$C_{33} = \gamma_{33}C_3$	$C_{p,3} = \gamma_{p,3}C_3$	C_3
Input	$C_{n,1}$	$C_{n,2}$	$C_{n,3}$		
Total	C_1	C_2	C_3		

The elements in the Table [3] can be mathematically represented in a set of equations as following.

$$\gamma_{11}C_1 + \gamma_{21}C_2 + \cdots + \gamma_{s1}C_s + C_{n,1} = C_1 \tag{29}$$

$$\gamma_{12}C_1 + \gamma_{22}C_2 + \cdots + \gamma_{s2}C_s + C_{n,2} = C_2$$

$$\gamma_{1s}C_1 + \gamma_{2s}C_2 + \cdots + \gamma_{ss}C_s + C_{n,s} = C_s$$

Eq. [29] can be written in matrix from as:

$$\gamma^T . C + C_n = C \tag{30}$$

Where γ is transaction coefficient matrix (square matrix) and C_n is the vector of the cumulative exergy of system inputs.

The vector of cumulative exergy of the products, Cp, can be calculated by

$$Cp = \gamma_p \cdot C \tag{31}$$

From Eq. [30] and [31] The vector of cumulative exergy of the products, Cp, can be calculated by

$$Cp = \gamma_p \cdot (I - \gamma^T)^{-1} \cdot C_n \tag{32}$$

The form of the generic allocation matrix Γ is then

$$\Gamma = \gamma_p \cdot (I - \gamma^T)^{-1} \tag{33}$$

“T” is the transformity matrix from Emergy analysis. The relation between ECEC and Emergy analysis will be illustrated in the next section. "I” is an identity matrix.

This network representation and algebra can be used for ICEC analysis. However, whether it can be used for computing ECEC depends on the allocation approach, as discussed next.

2.3.4. Allocation

Since most industrial and ecological processes have multiple outputs, it often becomes necessary to allocate or partition the inputs between multiple outputs.

Allocation in Fully Defined Networks

As shown in Fig. [12b], when the streams allocated according to this scheme are combined, their cumulative exergy can be added. This allocation approach relies on detailed knowledge of the network and outputs for allocation. Its benefits are that cumulative exergy follows laws of conservation, making the algebra quite straightforward, intuitive, and consistent with widely used network algebra.

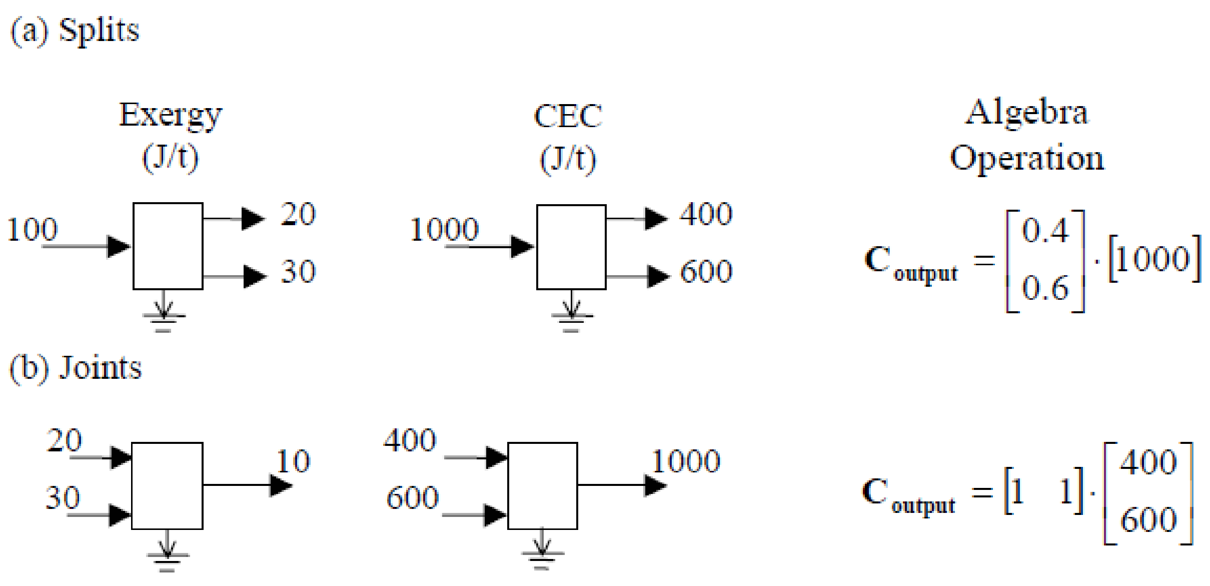

***Figure 12** Allocation in industrial systems: (a) for splits; (b) for joints.*

Allocation in Partially Defined Networks

The knowledge about the network structure and its outputs is not available. Fig. [13a] shows a system where only two outputs are fully defined, whether there are more outputs or not is unknown, portrayed by the triple dots between the known outputs. Even if the existence of additional outputs was known, it is often not possible to know their exergy content or network. This is usually the case with ecosystems since complete knowledge about the ecological network and its goods and services is not available. One strategy for such partially defined systems is to avoid allocation entirely and consider the exergy consumption of the process to be essential for making each product.

The main advantage of this approach is that the transaction matrix, $\boldsymbol{\gamma}$, can be defined by ignoring the unknown streams without losing information. However, since this allocation scheme violates conservation, special care is needed to avoid double counting when outputs from such systems are combined.

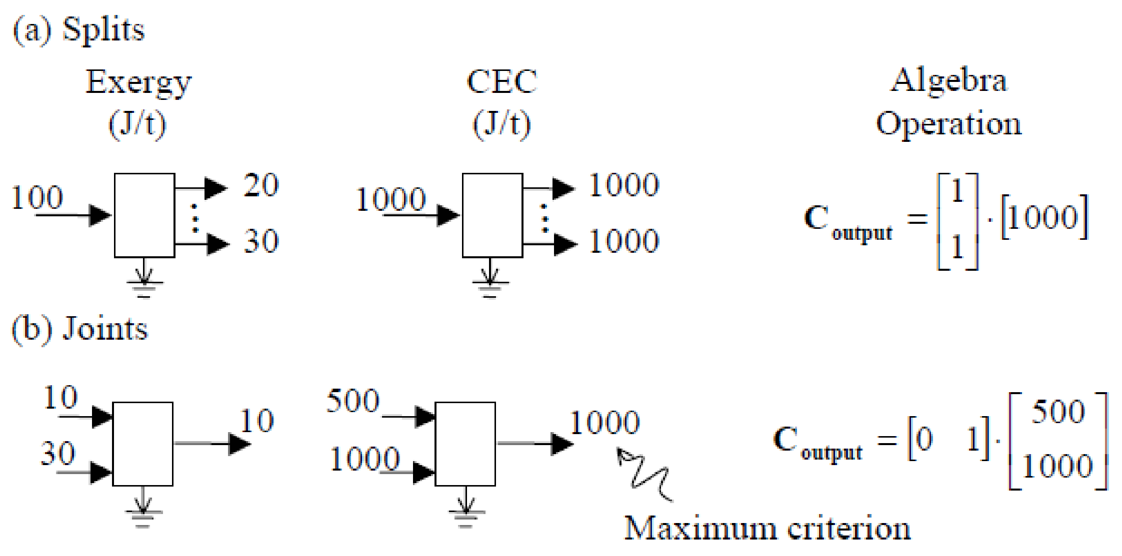

Figure 13 *Allocation in partially known systems: (a) for splits; (b) joints*

2.3.5. Relation between ECEC and Emergy

Computation of ECEC requires accounting of some ecological resources in term of Exergy which can be obtained by applying Emergy approach. To derive the relationship between ECEC and Emergy and conditions for their equivalence, matrix equations for emergy analysis of a network would be written. The Equation that links emergy and exergy may be written in matrix form as

$$M_p = \tau_p \cdot B_p \tag{34}$$

Where Mp and Bp are vectors of emergy and exergy and Tp is the diagonal matrix of transformities. For a network like that considered for ICEC analysis, Mp, may be calculated as

$$Mp = \Gamma'i \cdot Mn \tag{35}$$

Where M_n is the emergy vector of the natural resources and Γ′i is the allocation matrix for emergy analysis. Like ECEC analysis, Γ′i contains information about the allocation rule for emergy, that is, how emergy is assigned among splits, co-products, and joints. Similarly, the emergy of natural resources, M_n , can be calculated as

$$Mn = \Gamma'e \cdot M\boldsymbol{e} \tag{36}$$

The emergy and exergy of global inputs are related as

$$Me = \tau e \cdot Be \tag{37}$$

Where, Te represents the solar transformities of global inputs.

By using an overall allocation matrix, Γ′

$$Mp = \Gamma' \cdot Te \cdot Be \tag{38}$$

For ECEC and emergy to be equivalent, the following equation must be satisfied

$$Cp = Mp \tag{39}$$

The previous equations show that transformity is the reciprocal of the cumulative degree of perfection. This is

$$\tau_p = \eta_p^{-1} \tag{40}$$

Furthermore,

$$\Gamma \cdot \eta_e^{-1} = \Gamma' \cdot T_e \tag{41}$$

For a fair comparison, it is essential for both, ECEC and emergy to have the same analysis boundary that considers the same network of processes. Secondly, if the allocation rule used by emergy and cumulative exergy analysis is identical, then $\Gamma = \Gamma'$. under these conditions,

$$\tau_e = \eta_e^{-1} \tag{42}$$

Ecological cumulative exergy consumption and emergy are equivalent if the following are identical; Analysis boundary, Allocation method, and Approach for combining global energy inputs.

2.4. Extended Exergy Accounting (EEA)

The concept of EEA was coined in 1998 [41]. The attribute "extended" is a reminder that the resulting product cost includes materials, energy, and externalities, and that the calculation is done along the whole life cycle of the system.

Extended Exergy (EE) measures the amount of primary exergy absorbed by a system throughout its life cycle. In addition to material and energy flows, it includes externalities, all expressed in terms of exergy (Joules, or W if a flux is considered). EE is computed as the sum of:

- Exergy cost of materials and energy flows (renewable and non-renewable), absorbed by the system under consideration. This contribution is identical to the Cumulative Exergy Consumption (CExC) of material and energy flows.
- An externality term E_{Ext}, including labour, capital, and environmental cost contributions, expressed by means of their primary exergy equivalents, respectively E_L, E_C, E_E [42].

$$EE = CExC + E_{Ext} \tag{43}$$

$$E_{Ext} = E_L + E_C + E_O \tag{44}$$

$$EE = EE_{const.} + EE_{op} + EE_{dis} \tag{45}$$

In other words, the Extended Exergy absorbed by the system throughout its life span is equal to the sum of Extended Exergy contributions during its main life stages:

$$EE = (CExC + E_{Est})_{const} + (CExC + E_{Est})_{op.} + (CExC + E_{Est})_{dis.} \tag{46}$$

And each term can be calculated by direct integration over the corresponding time window.

$$(CExC + E_{ESt})_{const.} = \int_{t_0}^{t_{const}} (CExC + E_{Est})dt \tag{47}$$

It is obviously possible to express the Extended Exergy in specific terms: the extended exergy content (eec) is indeed defined as the extended exergy required for the generation of a single unit of product:

$$eec_i = \frac{EE}{n_i} \left[\frac{J}{kg}; \frac{J}{J}; \frac{J}{unit}\right] \tag{48}$$

n_i is the cumulative amount of the product i in the period of interest, expressed in units of mass, energy or number of units.

The calculation of the overall exergy resources use throughout the life cycle of the system is one of the key features of EEA. To do that there are some criteria need to be considered from both spatial and time domain. As Shown in Fig. [14]:

- Material and energy fluxes must cross system boundaries in their raw state, without having been subjected to any previous pre-processing. This implies that the "traditional" control volume should be expanded to include all the upstream phases up to the original reservoir.
- Labour and capital flows absorbed by the system are considered as primary resource flows.
- Both material and energy waste flows must cross the system boundaries at their respective zero exergy level. This means that the "traditional" control volume should be expanded in order to include all the "downstream" processes needed to reduce the exergy level of the effluents [43].

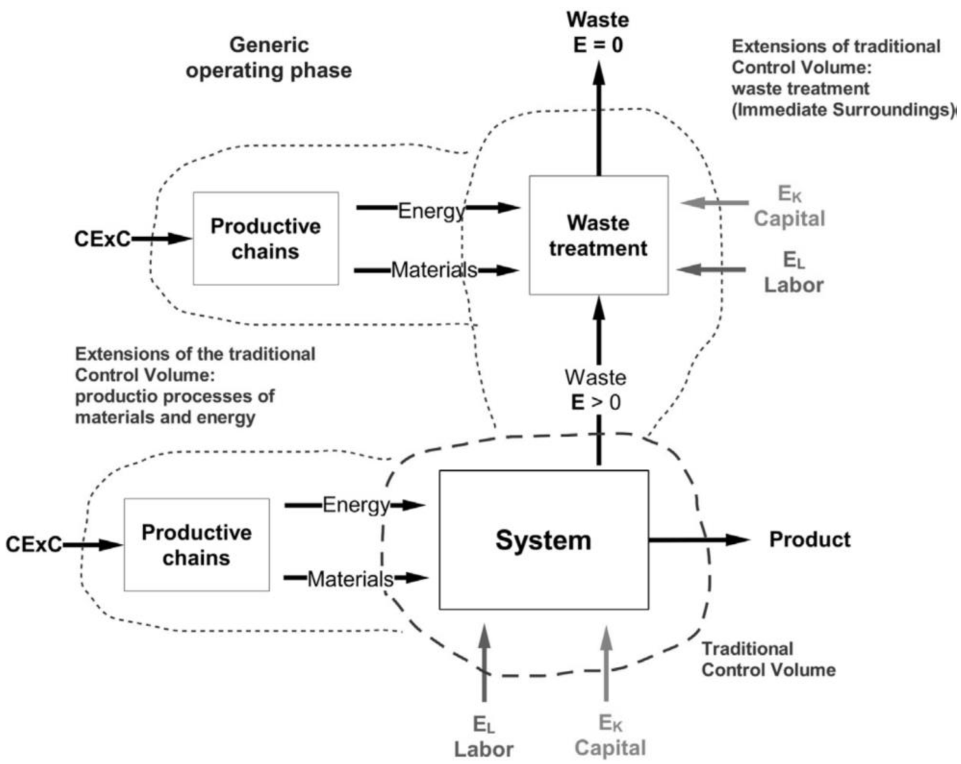

Figure 14 *The expanded control volume for EEA. Adapted from [41].*

2.4.1. The Labour externality

The calculation of the exergy equivalent of the human labour and capital flux is based on two assumptions. The first assumption is "In any Society, a portion of the gross global influx of exergy resources E_{in} is used to sustain the workers who generate Labour" [45]. The net exergy rate globally absorbed by the society E_{in} consists of: Exergy of the net solar radiation incident on the surface occupied by the society. Exergy of the net contributions related to raw material and primary energy (excluding solar) inputs. Cumulative exergy of the net material fluxes flowing into the society (fuel, food and all other material products).

The first postulate states that the primary product of the society is exergy embodied into labour EL, which is the exergy globally used by the entire population (workers + unemployed),E_{used}. This exergy flow rate is a fraction a of the net exergy input E_{in} :

$$E_{used} = \alpha \cdot E_{in} = E_l [J/year] \tag{49}$$

$$E_{dis} = E_{in} \cdot (1 - \alpha) [J] \tag{50}$$

This model assumes that all the members of a society, including those who consume resources without generating any work (minors, elderly, unemployed, etc.), thrive on the production of labour: they survive by using goods and services produced and supplied, in end effect, by the workers.

E_{used} can be calculated from the exergy flow diagram of the society under consideration [41].

$$E_{used} = f \cdot e_{surv} \cdot N_h \; [J/year] \quad (51)$$

Where f is a consumption amplification factor, N_h is the population numerosity and $\mathrm{e_{surv}}$ represent the minimum exergy amount required for the metabolic survival of an individual (≈1.05×107 J/ (person ×day) [55], corresponding to 2500 kcal/day per person).

In the absence of statistical data, it is possible to estimate the amplification factor by investigating possible correlations between well-established socio-economic indicators and the Total Primary Energy Supply of a country (TPES). In some of the first applications of the method, the Human Development Index (HDI) was adopted [46]:

$$f = \frac{HDI}{HDI_0} \quad (52)$$

Where HDI_0 is the Human Development Index of a pre-industrial society (≈ 0,055) [55]. the dimensionless coefficient (α) is called first econometric coefficient. It represents the fraction of primary exergy absorbed by the society and converted into labour (workhours).

$$\alpha = \frac{f \cdot e_{surv} \cdot N_h}{E_{in}} \quad (53)$$

The exergy equivalent of labour (ee_l). For a given society, if (Wh) represents the average annual working hours of one worker [h/ (year worker)] and $N_w$is the number of workers, the total number of workhours N_{wh}generated in a year is:

$$ee_L = \frac{\alpha \cdot E_{in}}{N_{wh}} \; [J/h] \tag{54}$$

$$N_{wh} = N_w \cdot Wh \; [h] \tag{55}$$

2.4.2. The Capital externality

The calculation of the exergy equivalent of the capital flux requires a second fundamental postulate: "The amount of exergy required to generate the net monetary circulation within a society is proportional to the amount of exergy embodied into labour" [45].

$$E_c = \beta \cdot E_L = \alpha \cdot \beta \cdot E_{in} \; [J/year] \tag{56}$$

Considering the simplified society shown in Fig. [14] which consisting of only two sectors, domestic (DO) and productive (PR). Two "circulations" can now be identified between these two sectors: the first is a material one (goods, services and workhours), while the second is monetary (wages, compensations and purchases). These two circulations, represented in Fig. [15], are mutually dependent: the labour flux from DO to PR, expressed in exergy equivalentE_L, is necessary for the production of goods and services; however, these products are made available to DO only because of the parallel monetary circulation required for their purchase. In this simplified model, PR "generates" a monetary flux equal to the workers cumulative wages (Y), which are in turn fully reinvested by DO by purchasing goods and services from PR. Notice that in this simplified model there is no monetary or material accumulation.

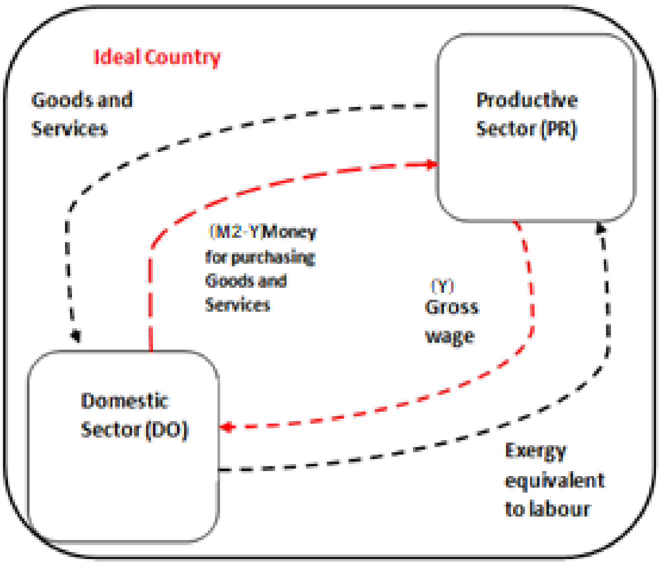

Figure 15 *Scheme of the internal structure of an ideal society. Adapted from [41].*

Eq. [56] states that the number of primary resources embodied in the net monetary circulation (the exergy fluxE_K) is related to the exergy of labour E_L through the coefficient β. This second econometric coefficient indicates the capacity of a society to generate monetary circulation in addition to wage compensation and is defined as the ratio between the monetary circulation due to financial activities (M_{Fin}) and the gross cumulative wages (Y):

$$\beta = \frac{M_{Fin.}}{Y}\ [ad.] \tag{57}$$

Where Y (Y = y. N_W. W) is the gross yearly wage of all the workers 'body [€/yr]. M_{Fin} is a fraction of M2 a monetary aggregate that represents, at a given time in the considered economic system, the total quantity of circulating money and financial activities which can perform the same functions of money. The second econometric coefficient in a simplified society devoid of financial activities would obviously be equal to zero, because the monetary circulation due to financial activities would be equal to zero. However, in current societies, β is always greater than zero, because of the extra monetary circulation generated by financial activities (M_{Fin}). So, the second econometric coefficient can be expressed as a function of circulating capital due to financial activities:

$$M2 = \mathrm{Y} + M_F$$

$$\beta = \frac{M2 - \mathrm{Y}}{Y} \tag{58}$$

β is defined as a ‘‘financial ratio’’ or ‘‘financial amplification factor compared to the gross cumulative wages’’. Indeed, from the definition it follows that the higher b, the higher the ability of the society to generate financially leveraged monetary circulation. Similarly, to α, β depends on the spatial context (geographical location) and on the considered time window (historical period and technological level), but also on some socio-economic parameters and the societal organization of the considered country.

It is possible to compute the exergy equivalent of capital (ee_c) as the ratio between the exergy that generates monetary circulation (E_c) and the global net monetary circulation of the society:

$$ee_c = \frac{\alpha \cdot \beta \cdot E_{in}}{M2} \; [J/€] \tag{59}$$

Values of α, β, ee_L and ee_k have been computed for 23 OECD countries and for 54 developing and emerging countries in [49].

2.5. Promises and problems of Exergy accounting approach

Every exergy-based approach has its advantages and its drawbacks. It even has its own spatial and temporal domain as shown in Fig. [16].

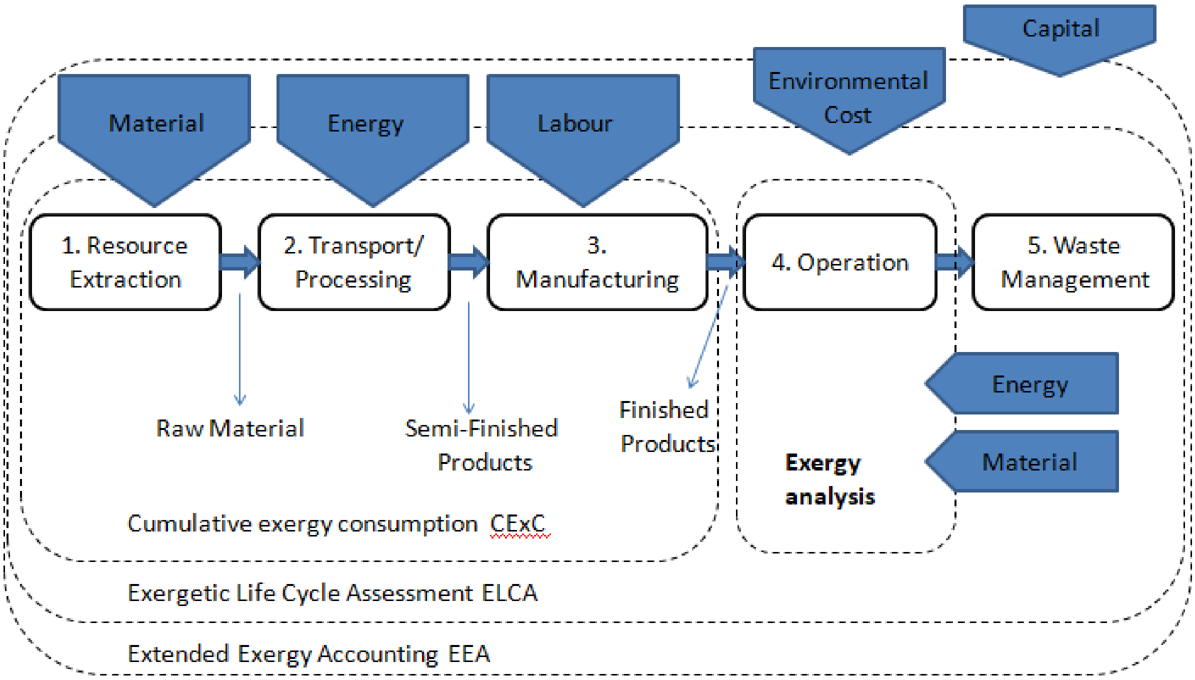

Figure 16 *Spatial and temporal domains of different approaches adapted from [71]*

Thermoeconomics (TE)

It is currently a standard tool in both academic studies and industrial applications because of its solid foundation and continues to provide substantial contributes to the improvement of the economic cost efficiency of energy systems.

However, TE is affected by some critical drawbacks [6]:

a. The assumption of a rigidly monetary basis introduces a strong dependence of the results on market considerations, which influence the monetary price structure (in a TE perspective, the monetary cost) of the Fuels (especially of the natural resources).

b. It is difficult to formulate a TE analysis of scarce resources, since TE considers as "fuel cost" the result of the flow rate of a certain input stream multiplied by the specific exergy of the flow, and the latter is assumed to be zero when the stream is directly extracted from the environment.

c. The evaluation of the costs associated with the environmental remediation activities suffers of the lack of a thermodynamically and physically correct link between the exergy of an effluent and its toxicity.

d. In a complex production chain, the exergetic efficiency of a component influences the performance of all other components, so that the final product cost is a non-linear function of the cost of all components, their efficiency and of the connectivity of the plant: a correct assessment of these effects on the optimal cost structure is inevitably depending on some "design decisions" made by the analyst (this is known as the "allocation problem" [6])

Emergy Approach

Emergy approach has some attractive characteristics. Among of these attractive characteristics are [31,32]:

- It provides a connection that connects economic and ecological systems. Since emergy can be quantified for any system, their economic and ecological characteristics can be compared on an objective basis that is independent of their monetary perception.
- Its common unit allows all resources to be compared on a fair basis. Emergy analysis recognizes the different qualities of energy or abilities to do work. For example, emergy reflects the fact that electricity is energy of higher quality than solar insolation.
- Emergy analysis provides a more holistic alternative to many existing methods for environmentally conscious decision making.

Emergy has been criticized for many reasons. The major criticisms of emergy analysis are discussed below [33,34].

- The emergy theory of value, as other theories of value based on energy and exergy focuses on the supply side and ignores human preference and demand. All the thermodynamic theories of value have been rejected by economists over the last several decades.
- There seems to be much confusion about the relationship between emergy and other thermodynamic properties, such as energy, exergy, enthalpy, etc. There is also some confusion

about the exact definition of available energy, denoted B. It is certainly not Gibbs free energy because not all of it is available for work.

- Emergy analysis has not considered the uncertainty in many of the numbers used to calculate the transformities. averaged transformity of industrial and geological processes are frequently used in specific case studies with no knowledge of the degree of certainty of the resulting output.
- Problems of allocation; The method used for partitioning or allocating inputs between multiple outputs makes the emergy algebra quite challenging. Allocation is probably the most confusing aspect of emergy analysis, particularly to engineers who are used to conservation equations, even for systems with recycle. Emergy algebra can be very sensitive to the level of knowledge of the system under study.

Ecological Cumulative Exergy Consumption

The calculation of the CExC of energy and material flows requires a rather detailed bookkeeping. Approximations are often necessary. ECEC method is conceptually close to the Emergy method, trying to expand the boundary over the ecosystem processes. Furthermore, practical applications of the methods are performed in a similar way. ECEC uses an analogous concept of transformity, called Ecological Cumulative Degree of Perfection (ECDP), to express the ratio between the exergy and the embodied exergy of products [36].

Even if ECEC approach has the advantage of using exergy as the numeraire, its formulation suffers from the same problems of Emergy analysis, mainly related to the allocation of exergy cost and to uncertainties caused by the lack of data for most of the processes that occur within ecological systems. Moreover, the formulation of this method does not encompass all the life cycle of the system: exergy requirements due to disposal of the product and the influence of recycling are not considered [37].

Extended Exergy Analysis

EEA may be considered as a step forward in evaluating the overall resource consumption of a generic system because it is able to include social, economic and environmental externalities expressed in homogeneous exergy terms and because it is founded on a life-cycle formulation. EEA offers a deeper insight than simple exergy analysis and all other exergy-based methods.

Furthermore, the extended exergy cost function can be used within the traditional and well formalized Thermoeconomic framework, replacing the economic cost function in order to evaluate and optimize the consumption of natural resources of a system. Indeed, some recent studies show that EEA may be used to analyse both traditional energy systems and complex systems (complex networks and societies) [41]. The results demonstrate that EEA is a tool for performing design and configuration optimization, and that its results may give additional insight to the analyses when compared to those of a thermoeconomic analysis.

After reviewing the Extended Exergy accounting method (EEA), some drawbacks that need further investigation have shown with a specific intent of indicating some high-priority research directions.

The Extended Exergy method needs a real standardization and formalization and in order to do that, some aspects needs to be considered for further investigation [42]:

- Choice of the system object of the analysis: definition of temporal and spatial boundaries.
- Definition of the relevant system parameters.
- Data collection, mass, energy, and exergy balances of the system/environment interaction, including the related material and energy supply chains.
- Exergy analysis of the country in which the life cycle of the considered system takes place: calculation of the exergy equivalents of labour (ee_L) and capital (ee_k).
- Calculation of Extended Exergy (EE).

The definitions of the exergy equivalent of labour and capitals needs some further investigation which must be performed with an open mind, perhaps reassessing the coherence of the simple socio- economic model hitherto adopted for the reference society.

3. The Thermoeconomic Environment Cost Indicator ($i_{ex\text{-}TEE}$) as a One-dimensional Measure of Resource Sustainability (Novel Definition)

It can be noted that an effort is under development in the literature to define resources sustainability indicators based on thermodynamic quantities, on exergy. Exergy is widely recognized as a proper tool for evaluating the resources required by energy systems [1-5] or by technological production systems in general [6-11]. In addition to the basic exergy analysis, an exergy cost accounting must be implemented [54-57] while dealing with complex, multi-component, energy systems with both direct and indirect exergy consumptions required for obtaining a certain product flow. Furthermore, when the goal is to assess the impact or the sustainability of the production system, the actual primary exergy resources, directly and indirectly, available for the production system itself have to be considered. The expectation is that an exergy-based sustainability indicator could encompass in a one-dimensional figure various aspect of sustainability, even if not all of them.

This Thesis first summarizes different exergy-based cost accounting approaches presented in the literature, highlighting the effort to include in the analysis a progressively more complete picture of the indirect effects and externalities of the production process, which may affect the sustainability of the process itself. Then, an extension of the previous cost accounting method is presented, based on the concept of the TEE. This is a consistent ultimate boundary of exergy cost accounting, where various exergy reservoirs, of limited content, are immersed in the zero-exergy matrix as shown in Fig. [17], but they remain separated from it because of some confinement constraints. Starting from this very simple but meaningful framework, the concept of bioresource stock replacement (BSR) cost is precisely defined, allowing the exergy cost evaluation of all biological resources used as production process inputs. Introducing the concept of BSR cost does not need any arbitrary hypothesis, or cost allocation rules not consistent with the input/output framework [58] that is a characteristic of the great majority of the cost accounting approaches presented in the literature. Moreover, it is consistent with the replacement cost of mineral resources presented recently by Valero and Valero [59], as an extension of the Thermoecological cost, historically introduced by Szargut [57,60]. Finally, the Thermoeconomic

Environment Cost (TEEC) is presented, and, on this basis, a new exergy sustainability indicator is easily defined, and its potentiality as a one-dimension measure of resource sustainability is discussed.

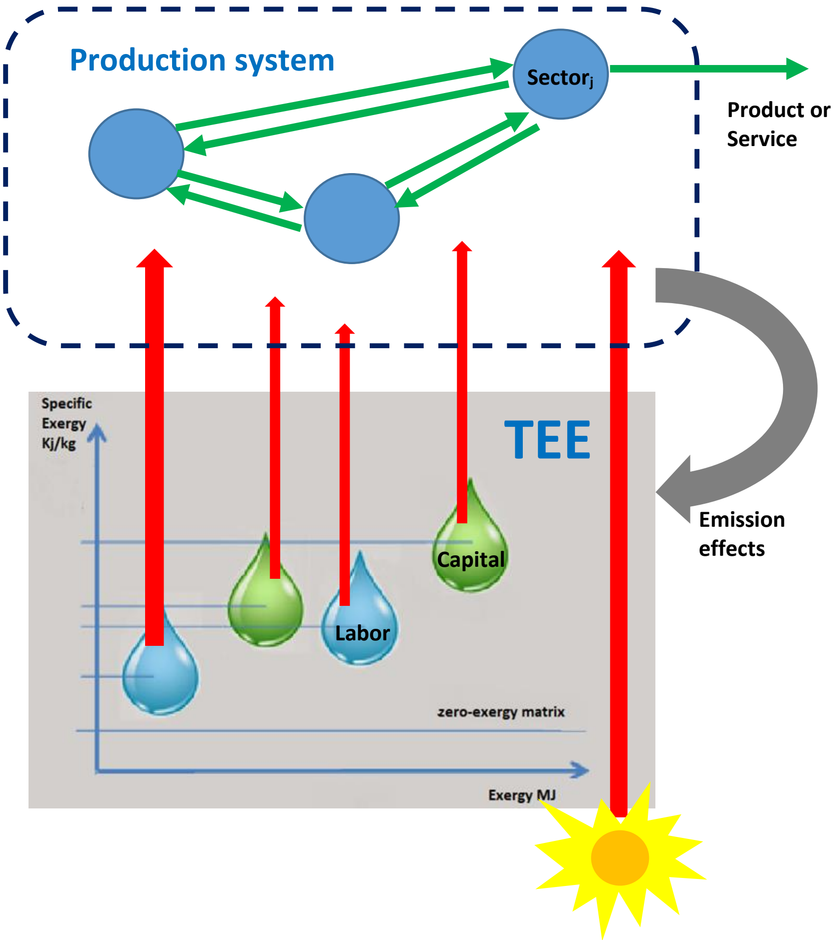

Figure 17 *A qualitative representation of the flows involved in the TEEC evaluation.*

3.1. An outlook to some sustainability indices in the literature

A critical summary of the previous effort for identifying exergy-based sustainability indicators can be found in [61], where the authors highlight the limitations of two approaches based on Thermodynamics in defining a proper sustainability index: the Emergy Synthesis and the Exergy Analysis. Agreeing with Kharrazi et al, the sustainability index proposed by the Emergy Synthesis [29,30] allows us to highlight important measurements of sustainability, but it does not consider any limit to the minimization of input Emergy consumption, implicitly assuming that a reduction is always possible and desirable, as well as a wider usage of renewable resources. In addition, the Emergy sustainability index is defined as a ratio [62] where the product of the yield and the input renewable resources is on the numerator, whilst the sum of the capital invested plus the input non-renewable resources, both multiplied by the capital invested, is on the denominator. The reasons for such a definition are not immediately evident; therefore, also its physical meaning is not clear, beyond the idea that higher product yield and a higher renewable input, at constant non-renewable and capital resource consumption, is a more sustainable condition, for a certain system.

in the same paper by Kharrazi et al. [61], the Authors recognize that recent methods based on exergy cost accounting (like the EEA) attempt to unify capital investment, human labour, and environmental resources into a common exergetic description. Nevertheless, they note that, in the exergy literature, no sustainability index, similar to the one defined by the Emergy Synthesis, has been presented. In fact, the latter does not consider only the strict (and arbitrary) control volume of the analysed system but attempts of considering also direct and indirect effects of system activities. On the other hand, Emergy cannot be obtained from a straightforward input-output approach, but a peculiar algebra has to be used, which implies a non-conservative nature of the Emergy itself.

Various exergy indexes claim to express sustainability [63], but they mainly relay on the exergy efficiency concept, without prescribing a specific control volume, or a pre-defined origin of the supply-chains that feed the considered production process, or component. This is the case, for instance, of the Depletion number (D_P) and the sustainability index (SI) shown by Rosen [64]. D_P is the complement to one of the exergy efficiencies, and the second is the inverse of the first one, i.e., they convey the same information of the exergy efficiency itself.

A different definition of the exergy sustainability index is used in [65], as the ratio of the exergy of the products and the exergy content of waste flows. Other indices are defined by Dewulf et al. [66] as the fraction of renewable energy in the total input (named the exergy renewability indicator) and the ratio of the in-input exergy and the sum of the same input exergy plus the expected exergy consumption for a complete abatement of harmful wastes from the process (named the environmental compatibility).

All these indices do make sense, but direct and indirect effects of system activities, outside the control volume of the system itself, are not systematically investigated, but they are simply supposed to be proportional to the exergy of some input, or output flow.

In the following, the most relevant properties expected for a sustainability index is presented, by critically combining and integrating the requirements highlighted:

a) It must be expressed by a - possibly simple - numeric expression and produce results that can be unambiguously ranked within two opposite limits.

b) It must be calculated based on intrinsic properties of both the process (the system that it refers to) and of the (local or global) environment.

c) It must be standardized in some sense, so that it may be used to compare different systems or different environmental conditions, or else different scenarios and/or time series for the same community.

d) It must be calculated based on an unambiguous, reproducible method under a well-defined set of fundamental assumptions.

e) It must comply with the accepted laws of physics.

3.1.1. Exergy cost accounting for assessing sustainability

When dealing with complex, multi-component, energy systems with both direct and indirect consumptions for obtaining a certain product, an exergy cost accounting has to be implemented besides the basic exergy analysis. Exergy cost accounting definition requires:

- cost allocation rules (input/output algebra by Leontief [58] are widely accepted, but other cost allocation rules may be found in the literature [67, 68].
- clear limits for the control volume, where the start of the exergy supply chains of the system is located, and where the unit exergy costs of all inputs crossing the limits must be known [69].

Some other additional conditions must be considered to use exergy cost as a sustainability indicator. The actual primary exergy resources must be identified, and the exergy cost of polluting emissions must be evaluated. There is wide agreement about cost allocation rules and in practice, all exergy-based costs must be allocated to the product. There is still some investigation to avoid what is called double accounting when a multi-products system has to be analysed or some other constraints come up. The conservative nature of the cost flows through the energy conversion system is important if the aim is to quantitatively evaluate the impact on the primary resources of goods or services, not only obtaining meaningful indicators. Moreover, to assess sustainability it is important to indicate the impact affecting the resources available at the present moment, not in the distant past time, so the time scale has to be defined properly. Even if the cost allocation rules are defined and consistent with conservative cost balances of all control volumes, the ultimate boundaries play an important role in exergy cost accounting and have to be consistent with assessing the impact in primary exergy resources of a product and service. The reference environment used in the basic exergy analysis cannot be identified with these ultimate boundaries of the exergy cost accounting analysis [70], because it is perfectly homogenous, its temperature and pressure cannot be modified, and it cannot be affected in any way by the interaction with the production system considered.

If the goal is assessing sustainability, not only obtaining a rational comparison among products or technologies, but additional conditions may also be summarized as:

- The actual primary exergy resources have to be identified, considering both renewable and non-renewable resources,
- The impact affecting the resources available now has to be assessed, not that in a distant past time,
- all exergy costs related to polluting emissions have to be evaluated, besides the exergy costs of the inputs.

It has to be recognized that the EEA defined by Sciubba [46-49] has achieved an important advance in this direction. It measures the amount of primary exergy absorbed by a system throughout its life cycle, even if without any special attention dealing with biological resources, which are accounted for at their exergy content. In addition to material and energy flows received directly and indirectly from Nature (where all the supply chains start), it includes externalities for capital investments, human labor, and polluting emissions, the latter calculated on a remediation basis, similarly to Dewulf et al. [66]. The exergy cost of the products, as well as the exergy efficiency of a process or a region [72, 73], calculated through the EEA approach, are certainly not limited to the only strict (and arbitrary) control volume of the analysed system.

3.2. Definition of the Thermoeconomic Environment (TEE)

The TEE is introduced as a consistent ultimate boundary for the exergy cost accounting, with the following objects [74]:

- overcoming drawbacks of the Reference Environment, used in the basic exergy analysis.

Some of these drawbacks are that the reference environment has no resources of energy or raw material that are required to be consumed to obtain a specific process or product. The reference temperature cannot be modified, which means that some phenomena, like global warming [75], cannot be accounted for; in addition, the reference environment is not affected by any polluting emissions from the production system.

- defining a framework consistent with the formulations of CExC and EEA.

CExC and EEA are milestones of the effort of including into the exergy accounting analysis a progressively more complete picture of the indirect effects and externalities of the production process. Some of the ideas developed in those approaches will be used in the following to define the proposed Sustainability Indicator.

- suggesting new options for a consistent exergy cost definition of all resources. As will be evident in the following, the framework of the TEE may help the definition of a proper exergy cost for the effect of polluting emissions from the production process, or for the indirect destruction of resources, including the living biomass.

The TEE is defined as a set of reservoirs, where different kinds of natural resources are confined. All of them are surrounded by the zero-exergy matrix (the dead state). Each available resource has a specific exergy content greater than zero as shown in Fig. [18].

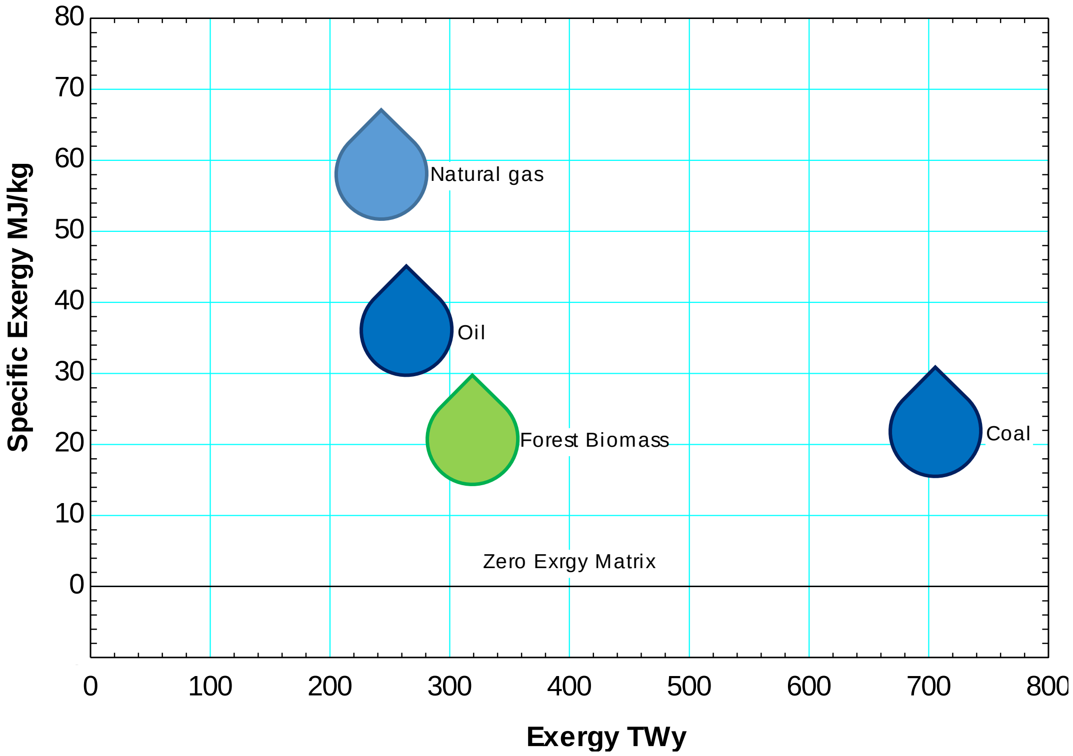

Figure 18 *A partial semi-qualitative representation of the TEE.*

From the previous definition, it can be easily inferred that the TEE is not "too big to be modified" by the interactions with the production processes because the amount of exergy in each reservoir is limited, and because of the confined conditions of the reservoirs can be compromised. In addition, to consider some real-world phenomena like the periodic oscillations of the availability of solar energy or global warming, which is on the run-in consequence of GHG emissions, it has to be recognized that even the zero-exergy matrix may change its temperature T° and composition.

3.3. Chemical Exergy calculation

The zero-exergy matrix may be defined as the reference state model introduced by Szargut [76,77]. It is based on the identification of a set of reference substances, whose specific chemical exergies can be determined as concentration exergy, with respect to an ideal mixture of gas at T°, P°. The chemical exergies of all other substances in the TEE can be calculated, considering reversible chemical reactions. Notice that, in this way, each crude fossil fuel and all other mineral resources, are not obtained as confined inside reservoirs, but they may be better regarded as obtained all together, i.e. mixed in a condition that may be identified as the Thanatia planet, introduced by Valero and Valero [59]. Notice also that additional exergy has to be consumed to obtain the resources in a confined way, as they are found in real-world mines or as they are regarded to be inside the TEE.

The specific exergy costs of each available resource inside the TEE are the basis of the accounting: specific exergy costs of each reservoir may be considered equal to 1, consistently with the hypothesis by EEA and CExC. This expresses the idea that a certain exergy stock of non-renewable resources is available in the TEE now, jointly with a set of exergy flows of renewable resources (including the renewable part of all partially renewable reservoirs).

3.4. The exergy cost of mineral resources

If the dynamic process allowing the exergy accumulation inside the reservoirs can be neglected, the assumption of specific exergy costs of each reservoir equal to 1 may be correct, even if a larger amount of exergy has been required in the distant past. For instance, when the accumulation process is very slow compared with the duration of the considered production process, like for natural fossil fuel, or other mineral reservoirs.

On the other hand, if a not-negligible dynamic exists inside the TEE, the exergy extraction from a certain reservoir may produce additional exergy destruction in other reservoirs. In this second case, two options can be identified:

- to extend the supply chain describing the indirect consumption of resources,
- to define a set of unit exergy costs, not equal to one, which is regarded as equivalent to the mechanism of additional exergy resource destruction.

In 2011, [79,80] Valero introduced the exergy replacement costs (ERC) and the model of Thanatia to assess the concentration exergy of mineral resources, based on their scarcity in nature [59].

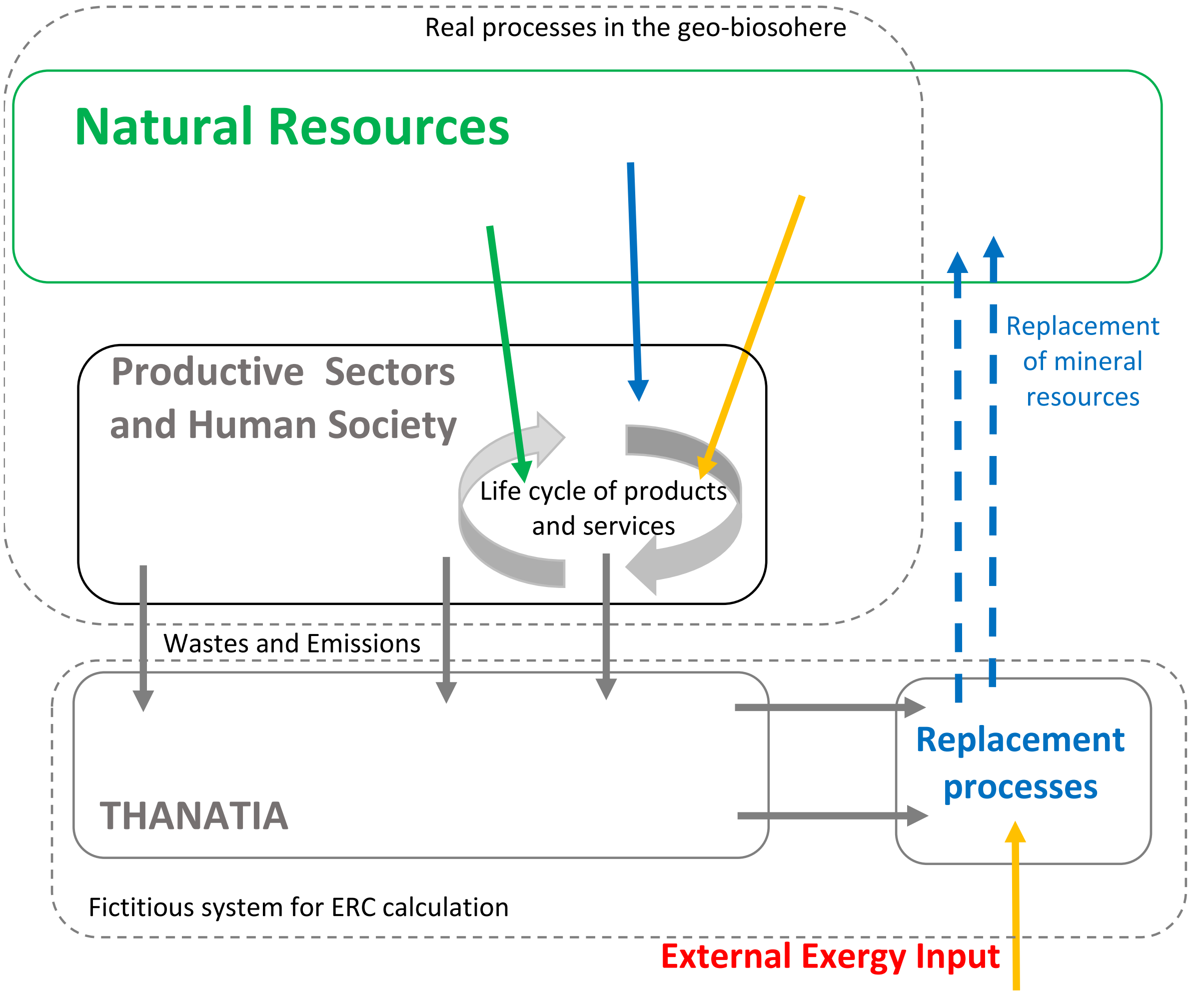

***Figure 19** "Cradle to grave to cradle" process for calculating the exergy replacement cost (ERC).*

In the TEE language, the proposal by Valero and Valero may be re-formulated by stating that, in the Thanatia planet, the confining constraints of all reservoirs have been destroyed, all minerals have been mixed, and have reacted with the zero-exergy matrix. Then, the ECR is the exergy required for producing a reservoir of a certain mineral resource, from the conditions defined for the Thanatia planet, by using real-world, irreversible technologies, as shown in Fig. [19]. This methodology has been introduced to assess the concentration exergy of mineral resources based on their scarcity in nature. The combination of the ERC concept with the Thermo-Ecological Cost method (TEC), originally proposed by Szargut, allows us to assess products considering the exergy associated with the consumption of non-renewable resources extracted directly from nature, taking their scarcity into account.

Notice that the only exergy input external to the geo-biosphere is solar energy (and possibly tidal and geothermal energy). Therefore, the ERC can be properly understood as the cost that should be paid to consider a non-renewable resource as if it were completely renewed by using solar energy, i.e. as if it were renewable, on a human time scale, like solar energy itself. It is worth noting that this interpretation makes ERC of mineral resources and the renewable energy in the input of a generic production process homogeneous, so that they may be added together without any inconsistency.

Mineral depletion is defined as a reduction in the availability of extractable or recyclable material that serves a given function in society, and that does not regenerate naturally. The ERC approach is based on the idea of using a resource two sequential processes have to take place. The first one is the creation of natural compound for instance hematite. The second one is to concentrate those compounds into viable deposits. Eq. [60] is a generic ERC calculation formula derived by Valero.

$$ERC_i = \{K_{ch_i} * b_{ch_i}\} + \{K_{c_i} * b_{c_i}\} \tag{60}$$

Where b_{ch_i} is the chemical exergy and b_{c_i} is the concentration exergy of i. K_{ch_i} and K_{c_i} are the dimensionless parameters depend on the chemical formation and concentration exergy cost when the best available technology is used.

4. The exergy cost of ecological goods (Novel approach)

Ecological Goods are material products developing from past and present ecosystem processes, such as fossil fuels, food, wood, and fiber; and from geological processes such as minerals. Human beings harvest and use them for economic activities. For instance, the real exergy of fossil fuel as an ecological good is not its intrinsic exergy represented in its Higher Heating value but also the exergy cost that was paid by the ecosystem to in the very far past to form it. The ecological goods are being depleted so rapidly and judging the sustainability of a system by only the conventional exergetic sustainability indicators that it takes only the chemical exergy of an element is very misleading approach.

Chemical exergy is not the same as the exergy required to re-capture and re-concentrate carbon dioxide, using current available technology, into a hydrocarbon that can be re-used. In fact, chemical exergy is the maximum amount of work that you can produce, in this case with a hydrocarbon. Although fossil fuels cannot be reproduced within an individual's lifetime with current best available technology, such as carbon capture and storage, the carbon cycle can be closed through photosynthesis as shown Fig. [20].

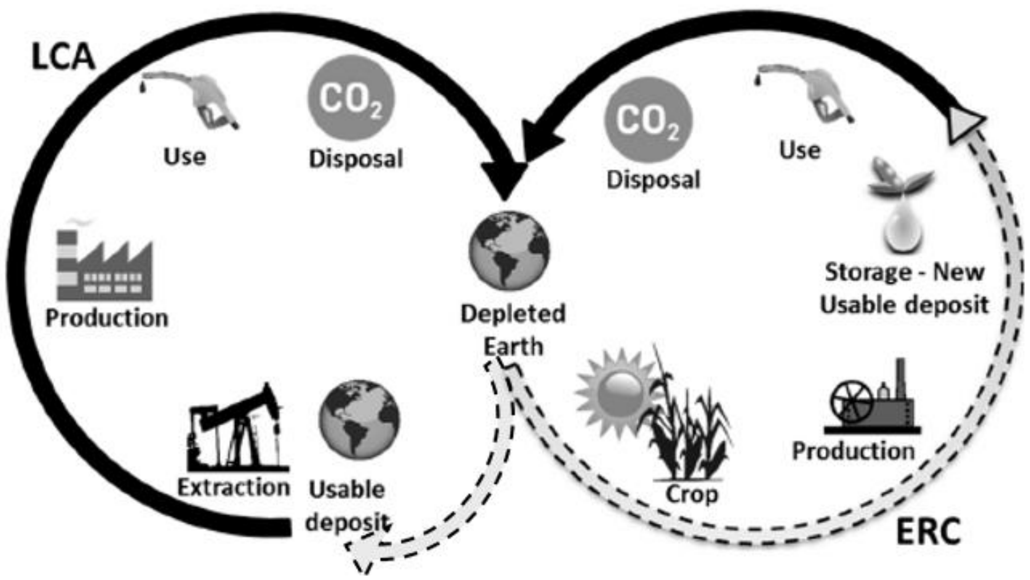

Figure 20 ERC through alternative bio-energy pathway.

The Exergy Replacement Cost (ERC) is an indicator that is used to determine the sustainability of non-renewable resource depletion. This new approach, via the cumulative exergy consumption (CExC), calculates the exergy replacement cost of photosynthesis and bio-energy production, as together they form the best available technology when it comes to closing the carbon cycle. This approach links together the "cradle to grave" to the "grave to cradle", concept that proposed by Valero, regulates the ERC calculations and enables comparisons between fuel and non-fuel mineral consumption. It also opens an argument as to the role of the ERC in sustainability debates and whether resource depletion should be a matter of geological legacy or material/energy services.

In literature, there are two approaches that introduce the exergy of ecological products which are Emergy analysis and Ecological Cumulative Exergy Consumption (ECEC) method by trying to expand the boundary over the ecosystem processes. Applications of these methods are performed in a similar way. ECEC uses an analogous concept of transformity of Emergy method, called Ecological Cumulative Degree of Perfection (ECDP), to express the ratio between the exergy and the embodied exergy of products (i.e., the invers of transformity). Even if ECEC approach has the advantage of using exergy as the numeraire, its formulation suffers from the same problems of Emergy analysis, mainly related to the allocation of exergy cost and to uncertainties. The latter are caused by the lack of data for most of the processes that occur within ecological systems, a lot of them being in a far past, when the driving forces in the geo-biosphere were completely different from now, and certainly they cannot be identified with the exergy resources we aim to save. Moreover, the formulation of this method does not encompass all the life cycle of the system: exergy requirements due to disposal of the product and the influence of recycling are not explicitly considered, at least in the original formulation.

The frame of the TEE offers an alternative for the evaluation of the exergy costs (greater than one) of the products of biological systems, similar to the Exergy Replacement Costs of the mineral resources and consistent with the EEA approach. In this case, an extension of the system is considered. Its function is to replace the stock of the bioresource reservoir in the TEE, if the stock has been affected by the operation of the system. In fact, if the bioresource is consumed at an extraction rate lower (or equal) to its growth rate, the stock is not affected and the input to the production system can be regarded as completely renewable, like solar radiation, and its exergy cost can be the same of the solar radiation (one). On the contrary, if the extraction rate is greater than the growth rate, the exergy stock of the TEE is affected and the extended system has to cultivate the ecosystem, for producing the biomass required for replacing the original stock. The bioresource stock replacement cost (SRC) can be calculated because the inputs of the extended system are obtained at known exergy costs. The solar radiation has a cost equal to its exergy (as in all the approaches considered), the necessary biological input from the same reservoir can be regarded as extracted from the fully renewable part, without affecting the stock, labour and capital can be accounted for at their exergy equivalent and all required mineral resources at their Exergy Replacement Costs. Then, the total cost of the considered bioresource is equal to its exergy, plus the stock replacement cost, resulting in a unit exergy cost greater than one, to take properly into account the interaction of the biological process with the production system considered.

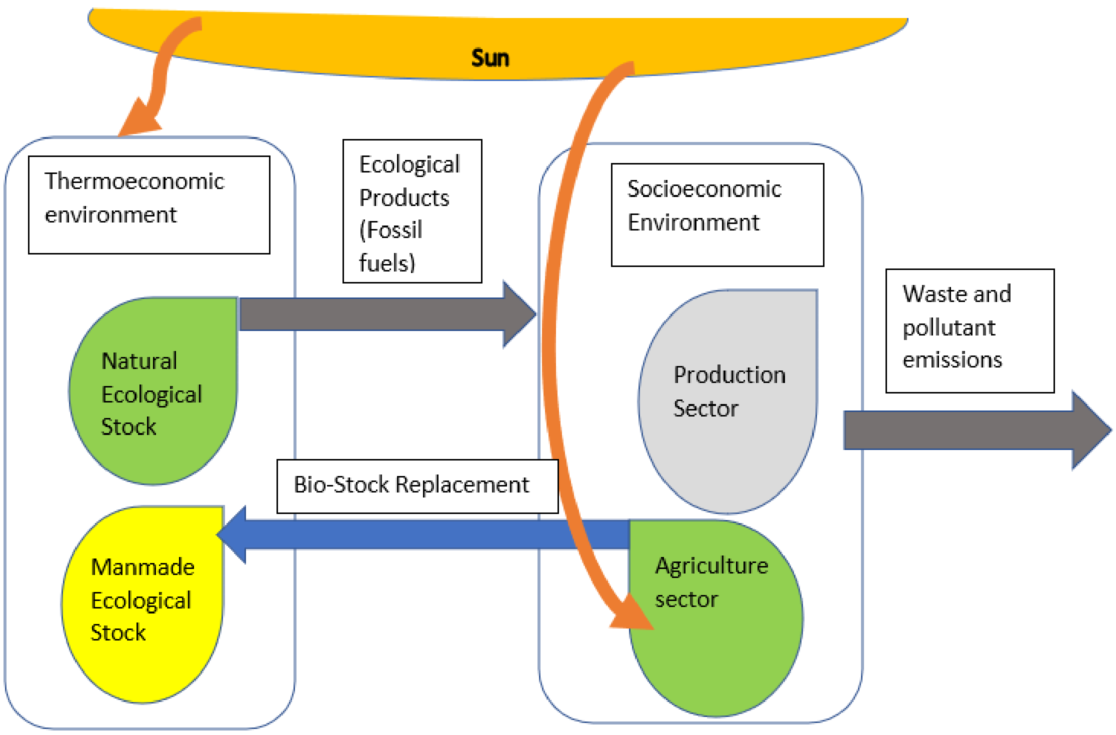

Figure 21 *The concept of Bioresources Stock Replacement Cost*

The frame of the TEE offers an option for evaluating the exergy cost of products of biological systems. As shown in Fig. [21], a fictitious extension of the system is considered with the function of replacing the stock of the bioresource reservoir, analogously with the replacement processes considered in the definition of the ERC of mineral resources. The object is to stay as close as possible to the latter methodology. But unfortunately, the ultimate wastes produced by the usage of biological substances are carbon dioxide, water, and very few other elements, so the replacement processes of the original resources (forests, agriculture fields, ecosystems, etc.) cannot be defined based on actual technology.

4.1. Methodology

To calculate the ERC of a given biological products i.e., fossil fuel, the CE_xC has to be obtained through LCA, of its bioproduct equivalents from "solar radiation to fuel". The second generation of Bioproducts is included within the "solar radiation to crop" and the "waste to fuel" scope. The third generation of Bioproducts is excluded because no exergy calculation for bioproduct production exists that may work with the parameter established within this method.

To obtain the CE_xC calculations, an extensive literature review has been done in order to collect CE_xC values derived from the production of bioproducts alternatives for fuel and non-fuel purposes. Large number of studies have been found within literature that cite Bioequivalents for natural biological products from different Bio-resources as shown in the following Table [3]. None of these studies consider solar radiation as an input to the bioproduction system and all start at the "Crop to Fuel" stage. This ignores the role of the sun in producing the crop and the role of the plant to convert such radiation along with carbon dioxide, into biomass through photosynthetic mechanisms.

Table 3 *Fossil fuel Bio-equivalent and Bio-source. Adapted from [83].*

Fossil Fuel	Product	Reference information	
Oil		Bio-Equivalent	Bio-Source
	Gasoline	Bioethanol	Corn, spent barely sweet sorghum, sugarcane, whey, potatoes, grass, and non-specified biomass
	Diesel and Jet Fuel	Biodiesel	Rapeseed, sunflower, palm oil, microalgae, and soybean
	LPG	Bio-SNG	Wood
	Kerosene	Used cooking oil	Cooking Oil
	Polymers	Bio-PET	Wheat, rapeseed
	Asphalt and Coke	Biochar	Wood

	Others	Methanol	Sawdust, sewage sludge biomass, wheat
Natural Gas	Natural gas	Biogas	Argo-waste, sewage sludge, grass, biowaste
Coal	Charcoal	Biochar	Wood

As it has been already mentioned before, The cumulative exergy consumption is the sum of all exergies for all stages within the system, for all renewable and non-renewable natural resources. The cumulative degree of thermodynamic perfection (η_x) is calculated as a ratio between the intrinsic exergy of bio-product and the calculated cumulative exergy consumption (C_{ex-x}).

$$\eta_x = \frac{B_x}{C_{ex-x}} \tag{61}$$

The exergy cost of a given product x (k_x) can be computed.

$$k_x = \frac{1}{\eta_x} = \frac{C_{ex-x}}{B_x} \tag{62}$$

The total k_x value is split into four main components biomass and non-biomass derived energy (fossil fuel and renewable resources, excluding biomass), water, and mineral. This helps to recognize the contribution of each input in the final output, which in this case is a bio-product. It also enhances the previous Exergy Replacement Cost method, which only accounts for energy inputs and ignores non-energy inputs (water, non-fuel minerals and non-energy uses of fuels such as plastics).

It is important to note that in the case of crude, there is more than one Bio-alternative as shown in Table [3]. Each fraction of the crude oil is used in different technologies that provide services to society. And hence, a weighted exergy cost, as shown in Eq. [63], is applied to account for the sub-products that comprise an average barrel of oil:

$$k_j = \frac{\sum_n f_n * k_x}{\sum_n f_n} \tag{63}$$

Where K_j is the weighted exergy cost of fuel (j), f_n is the fraction of product (n) that can be obtained from fuel (j), and k_x is the exergy cost of the bio-equivalent of product (n). The average decomposition of the products obtained from a barrel of oil corresponds to: gasoline 47%, diesel 23%, jet fuel 10%, liquefied petroleum gas (LPG) 4%, asphalt 3% and other products 13% [83].

Within the calculation of CExC for Bioproducts, Agricultural processes have the highest share to their (k) value. The average (k) value of different bio-products evaluated from “Crop-to-fuel”, represented in MJ of natural resources consumed (CExC) per MJ bioproduct is presented in Table [4].

There is huge variation between the (k) values for bio-energy carriers as they depend on the type of crop or waste used in the production. Bioproducts that are generated from waste have the lowest values because the exergy consumed before the disposal was assigned to the crop´s primary use.

Table 4 *Exergy cost of bioproducts from crop to fuel. Adapted from [93]*

Fossil Fuel	Product	Bio-Equivalent	Average (k)	Min (k)	Max (k)
Oil	Gasoline	Bioethanol	6.93	1.91	12.56
	Diesel and Jet Fuel	Biodiesel	5.70	1.94	11.97
	LPG	Bio-SNG	2.24	2.19	2.29
	Kerosene	Used cooking oil	1.32	0.67	1.97
	Asphalt and Coke	Biochar	3.64	-	-
	Others	Methanol, Oil	14.08	13.78	14.38
Natural Gas	Natural gas	Biogas	3.00	0.87	6.73
Coal	Charcoal	Biochar	3.64	-	-

There are min and max value for k because there are different Bio-Sources for the same Bioproduct as it has been shown in Table [4]. For instance, the lowest cumulative exergy of bioethanol when it is produced from corn and the highest value from potatoes. For Biodiesel, the minimum value corresponds to soybeans and the maximum to rapeseed. For Biogas, the highest value is derived from grass and the minimum value from biowaste.

4.2. Extraction Rate

If the bioresource is consumed (or indirectly destroyed) at an extraction rate (ε) lower than its natural growth rate in the reservoir (δ), the stock is NOT affected and the input to the production system is regarded as completely renewable (specific exergy costs equal to 1). If instead, the extraction rate is greater than the growth rate ($\varepsilon > \delta$), the fictitious extension of the system has to cultivate the ecosystem to replace the original stock. The BSR cost (C_{ex-BSR}) can be calculated because all the input costs of the extension of the real system are known:

- Solar energy, and other renewable resources, have a unit exergy cost equal to one,
- All non-renewable resources can be evaluated at their exergy cost, including indirect consumption and the ERC of the mineral resources,
- The capital and human work can be evaluated at their Exergy equivalent, with one of the methodologies previously outlined.

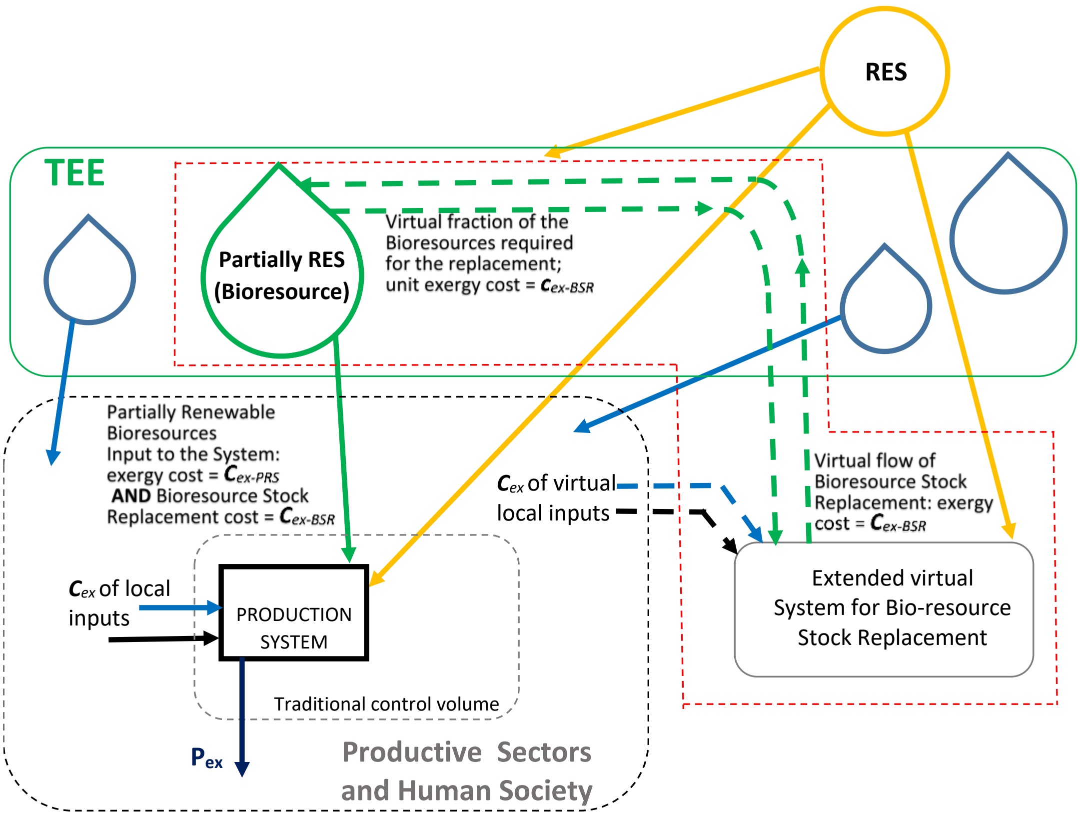

Figure 22 *Alternative more detailing Scheme of Bio-Stock replacement Cost.*

Notice that even a fraction (ρ) of the bioresource considered has to be virtually extracted, to be used as an input of the extended system for the bioresource replacement. This is because the living substance cannot be obtained from products of the economic sectors with actual technologies, without using some living input, too. The unit exergy cost of this flow has to be regarded as the same as the BSR, without introducing any problem in the calculation of the latter, based on the usual rules of the exergy cost accounting. This assumption is equivalent to considering a bifurcation of the virtual flow of BSR in two parts, one for the actual replacement and one for recirculating back the input required by the virtual system. This cost allocation rule in bifurcating flows has to be regarded as a well-consolidated result in the field of Thermoeconomics [82]. Moreover, it can be easily noted from Fig. [22] that the BSR cost can be inferred from the cost balance of the sub-system inside the dotted red line, without the need of explicitly knowing the cost of the bioresource recirculated back as input to the virtual system. In fact, the unit cost of the bioresource consumed by the production system, disregarding the stock replacement, is known and is equal to its chemical exergy (consistently with EEA).

It is worth noting that, if the extended system for BSR is considered, the differential equation governing the bioresource stock decline Eq. [64] is replaced by the differential Eq. [65]:

$$\frac{dM'}{dt} = (\delta - \varepsilon)M'_0 \tag{64}$$

$$\frac{dM'}{dt} = [\delta(1-\rho) - \varepsilon - \rho]M'_0 + \frac{dR}{dt} = 0 \tag{65}$$

Where *dR/dt* is the flow of bioresource replacement allowing a constant value M'_0 of the bioresource inside the reservoir to be maintained. Therefore, it can be easily obtained that:

$$\frac{dR}{dt} = M'_0[\varepsilon - \delta + \rho(1+\delta)] \tag{66}$$

$$\rho = \frac{(\varepsilon - \delta)}{(k - \delta)} \tag{67}$$

The parameter ρ in the last equation can be more properly understood as the fraction of the whole M, where a growth rate ($k > \varepsilon > \delta$) has to be obtained thanks to the additional local inputs coming from the productive sectors and additional renewable energy resources. The last two terms, evaluated at their proper exergy cost, constitute the BSR cost of the partially renewable input consumed by the production system.

4.3. The Exergy equivalent of capital and human work

In the EEA, Externalities can be assigned "equivalent exergy values", under a set of assumptions [41,42]. The more recent proposal by Rocco and Colombo [81] may be regarded as an attractive alternative, directly derived from the input/output algebra by Leontief [58]. In this approach, the interactions among the sectors of the whole production system are described by the monetary magnitudes usually adopted in the economic analysis. Then, the exergy evaluation of each flow in the model is obtained considering the exergy of all inputs coming from the environment and feeding the sectors (the nodes) of the production network. In this way, the exergy equivalent of capital has not to be evaluated explicitly, and (if it is evaluated later) the result may be different for the different production sectors considered.

As far as the exergy evaluation of human work is concerned, the approach suggested by Rocco and Colombo [81] is a direct extension of their exergy input/output analysis. The Human labor production sector is embodied as an additional sector, without the need of any arbitrary assumption, as is schematized in Fig [23]. This sector supplies the required human labor to all the others (only two big sectors, final goods production, and intermediate goods production are shown in the picture) and received from them (from the final goods production sector) all the necessary inputs for human labor production. Obviously, additional information is required, the quantitative evaluation of the inputs required by the human working activities from each one of the other sectors and, likewise, the human working hours required by each of them.

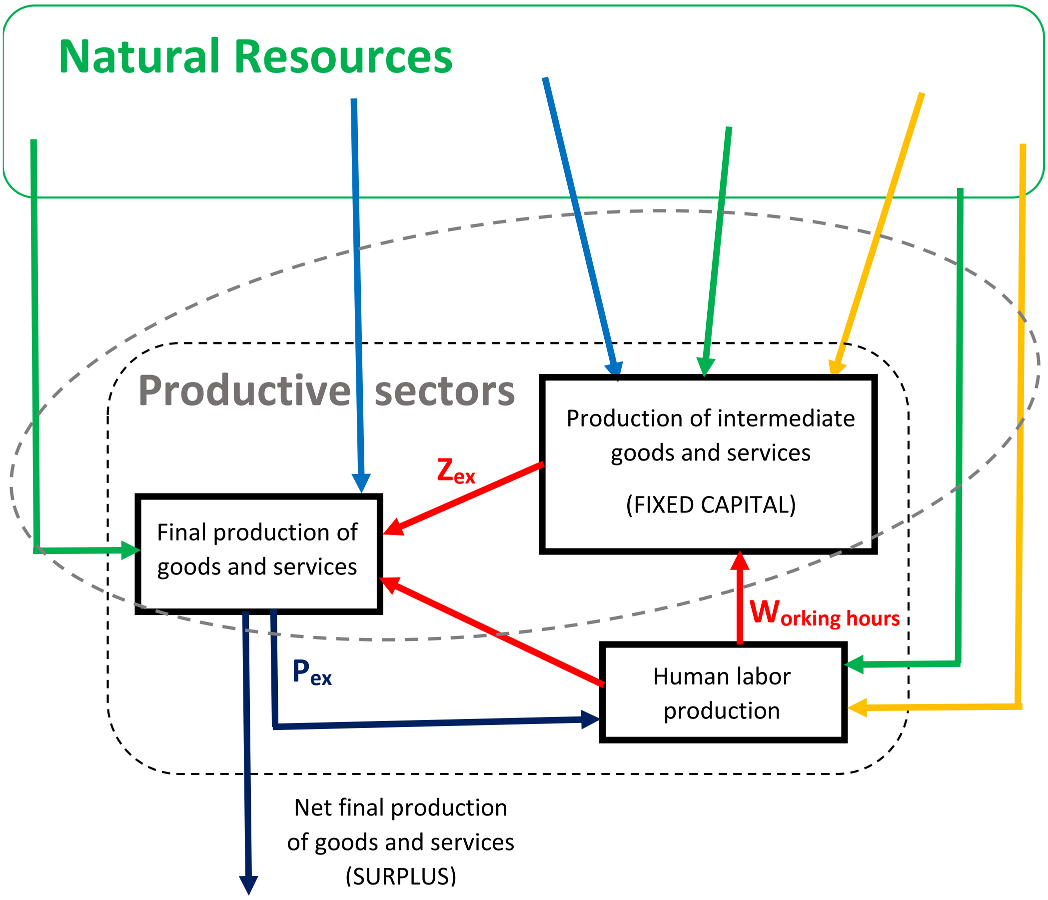

Figure 23 *Schematic of the sub-system introduced by Rocco, E. Colombo for the internalization of human labour in embodied energy analysis. Adapted from [41]*

4.4. The exergy evaluation of polluting emissions

For assessing polluting emissions, the exergy remediation cost has been suggested in the literature by the CExC and the EEA. In the EEA, both direct and indirect exergy consumption during the overall system operation and to support system decommissioning are considered, consistently with the LCA approach [47]. The ecological cost of polluting emissions is calculated on a remediation basis, by introducing a fictitious extension of the system, where the waste treatment process is completed, or entirely performed, as shown in Fig. [24].

It is worth noting that the remediation cost for neutralizing the chemical and physical exergy of waste (the cost actually incurred plus the virtual one) may be the same whether waste treatment strategies are applied or not. Treatments are required to convert all wastes into a flow with temperature and composition similar to those of the zero-exergy matrix of the TEE, but the not incurred part of it is performed in a fictitious way, inside the extension of the system. The cost for the actual treatment is generally even higher because the real processes are less efficient than the virtual ones. The result is that a highly polluting plant may appear less resource-consuming (more sustainable) than a plant that obtains the same product cleanly.

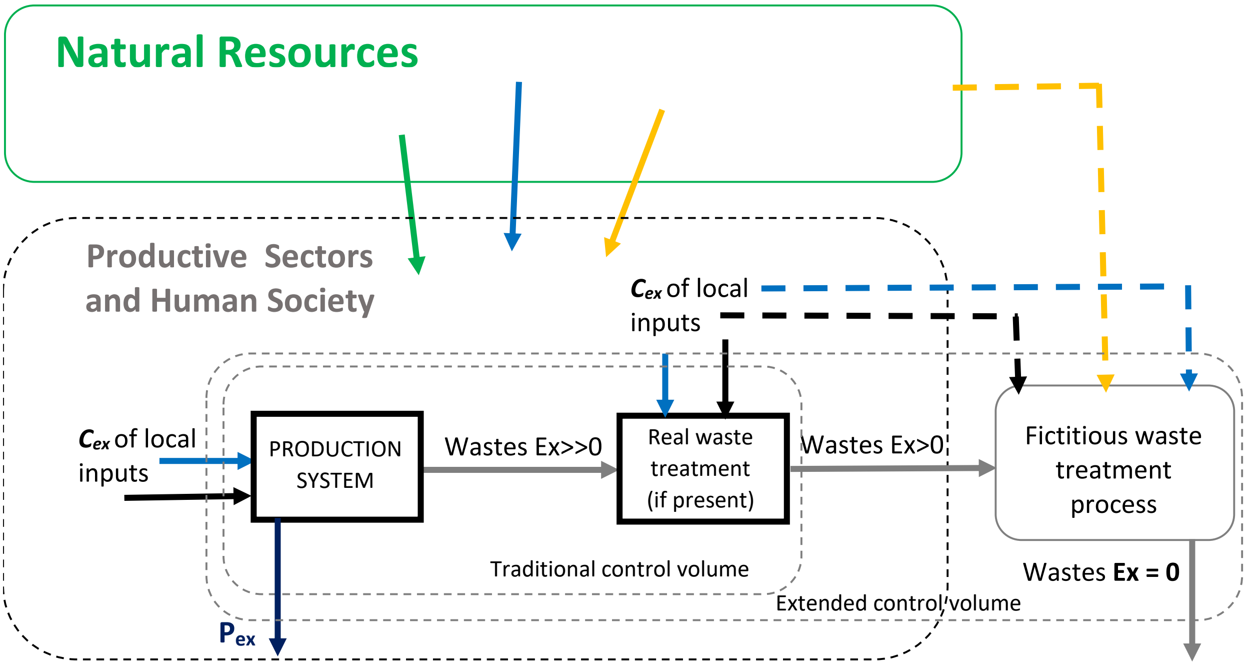

Figure 24 *The extended control volume for exergy cost evaluation of waste and pollutant emissions.*

In an alternative approach, the actual exergy cost of polluting emissions can be defined in the frame of the TEE, as the real exergy stock depletion produced by the polluting emissions in the whole TEE, in consequence of the following causes:

- the destruction of the confine restrictions of reservoirs,
- the variation of the zero-exergy matrix temperature, or composition,
- the dilution of substances inside the reservoirs, reducing their concentration,
- the indirect destruction of the (living) biomass stock inside the reservoirs.

In this way virtuous plants, which effectively include the emission neutralization system, may have a specific exergy cost of products lower than polluting plants, highlighting that the former have lower consumption of resources (i.e. they are more sustainable).

4.5. The Thermoeconomic Environment Cost Indicator (iex-TEE) calculation

Putting together all previous considerations, the TEEC can be calculated as follows:

$$\boldsymbol{C_{ex-P}} = \sum \boldsymbol{C_{ex-RES}} + \sum (\boldsymbol{C_{ex-PRS}} + \boldsymbol{C_{ex-BSR}}) + \sum (\boldsymbol{C_{ex-NRS}} + \boldsymbol{C_{ex-Rep}}) \tag{68}$$

Where:

$\boldsymbol{C_{ex-P}}$ is the TEEC of the product P,

$\boldsymbol{C_{ex-RES}}$ is the Exergy cost of the product P, considering only RES.

$\boldsymbol{C_{ex-PRS}}$, $\boldsymbol{C_{ex-NRS}}$ are the Exergy cost of the product P, considering only Partially RES, or Non-RES, respectively,

$\boldsymbol{C_{ex-BSR}}$, $\boldsymbol{C_{ex-Rep}}$ are the Exergy cost of the product P, considering only the exergy BSR cost of Partially RES, or the ERC of mineral non-RES, respectively.

As shown in Fig. [25], the flows extracted from the TEE have to include both direct inputs and all the other real exergy stock depletions in the whole TEE because of polluting emissions. In this context, in addition, an exergy-based sustainability indicator easily arises, named $\boldsymbol{i_{ex-TEE}}$, as the ratio between the exergy cost, calculated ignoring the ERC of non-RES and the BSR cost in the numerator and the total exergy TEEC, calculated taking all terms into account, in the denominator.

$$\boldsymbol{i_{ex-TEE}} = \frac{\sum \boldsymbol{C_{ex-RES}} + \sum \boldsymbol{C_{ex-PRS}} + \sum \boldsymbol{C_{ex-NRS}}}{\boldsymbol{C_{ex-P}}} \tag{69}$$

The exergy resource sustainability index $\boldsymbol{i_{ex-TEE}}$ is equal to one in the ideal case where all direct and indirect consumptions are in the form of RES, while it is internal to the 0-1 interval in all real cases, where both RES and Non-RES are consumed.

The index $\boldsymbol{i_{ex-TEE}}$ may approach one only if resources with a very low ERC or BSR cost are consumed, i.e. if all non-RES or partially RES possibly consumed are non-rare. It is worth noting that the recycling of materials reduces the value of both the ERC of mineral resources and the BSR cost, increasing the value of the proposed exergy-based sustainability indicator.

The index $\boldsymbol{i_{ex-TEE}}$ may approach zero when the primary inputs extracted from the TEE have a very high ERC or BSR cost, i.e. when rare mineral resources are consumed, or rare biological species, or even whole ecosystems, are destroyed, even if their exergy content were small.

Let's consider that EEA is the starting point for calculating the TEE Cost and the related resources sustainability indicator. In this case, the exergy equivalent of Capital and Labor are taken into account through the procedure suggested by Sciubba. Otherwise, the approach suggested by Rocco and Colombo may be followed. Notice that, in the latter case, the exergy equivalent of Capital is implicitly taken into account and could be calculated later.

If solar energy, as well as other renewable and partially RES, were properly considered, the total cost obtained in this way should be the sum of ($\boldsymbol{C_{ex-RES}} + \boldsymbol{C_{ex-PRS}} + \boldsymbol{C_{ex-NRS}}$) in Eq. [68]. The exergy cost of the BSR ($\boldsymbol{C_{ex-BSR}}$) of the biological products used as input of the production process has to be evaluated, following the frame shown in Fig. [20] and by using some additional information coming from the fields of agriculture and forest cultivation.

The $\boldsymbol{C_{ex-Rep}}$ of about all mineral resources consumed can be found in the papers by Valero [78, 79].

For what concerns the effect of polluting emission calculates EEA calculate this effect based on the "exergy cost of remediation" . In the thesis, it is suggested that the actual exergy depletion of the TEE should be calculated, because of direct and indirect effects. To proceed in this way, the "exergy cost of remediation" should be eliminated from the total accounting of the exergy cost of the product, if the remediation technologies are not actually put in operation. Then, an inventory should be compiled of the depletions in the TEE, in consequence of the polluting emissions of the production process in hands. The results of a LCA of a similar process, taken from the literature, may be used as a first attempt. Finally, the depletion of each reservoir should be estimated in terms of its exergy cost, including the exergy cost of the temperature in zero-exergy matrix. Notice that the depletion of mineral reservoirs has to be accounted for at a cost $\boldsymbol{C_{ex-NRS}} + \boldsymbol{C_{ex-Rep}}$, while the depletion of reservoirs of biological products at a cost $\boldsymbol{C_{ex-RES}} + \boldsymbol{C_{ex-BSR}}$. In this way, the effect of polluting emissions may affect all terms in Eq. [68] and [69] At this point, an evaluation of each one of the five terms on the right-hand side of Eq. [68] would be obtained and the indicator in Eq. [69] could be calculated.

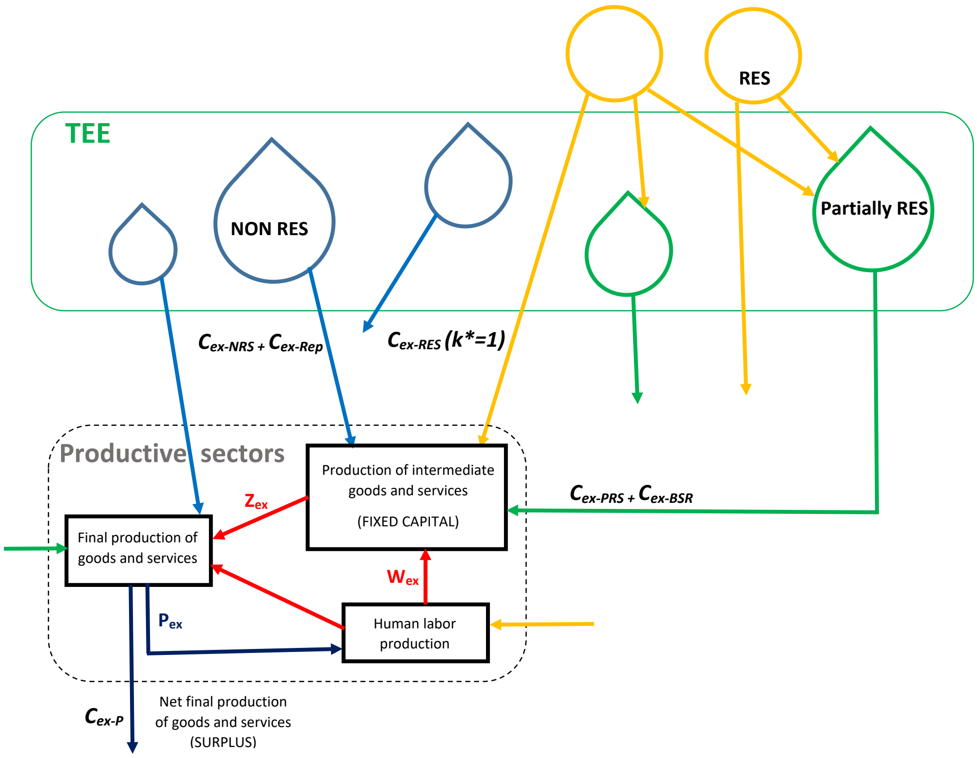

Figure 25 *Illustrative sketch of the procedure for the calculation of the TEE cost and the sustainability index.*

5. Case Study

Fossil fuels account for more than 80 percent of the world's primary energy consumption and their demand, corresponding to the International Energy Agency [94], British Petroleum [95] and the International Panel of Climate Change [96], will increase in order to meet societal demands. Such needs are increasingly powered by an growing global economy fed by the developing world's population growth. This has led to debates concerning the sustainability of societal preferences and a linear economy built on the argument that technological advancement will enable infinite growth.

Undoubtedly, conventional fossil fuel deposits are decreasing, leading to more unconventional extractions with ambiguous impacts on the environment and with a limited extension of resource availability, as can be seen in peak fossil fuel calculations.

According to [97,98], global coal, natural gas, and oil production, was 187 EJ/year (2012), 113 EJ/year (2008) and 170 EJ/year (2012) respectively. Their peak fossil fuel "best estimate" for all types of coal is 245.9 EJ/year, peaking in 2021, whilst for conventional oil the peak is expected to have occurred in 2006 at 167 EJ/year. The conventional natural gas peak is projected to occur in 2037 at 134.8 EJ/year.

The overall global fossil fuel production not only reducing, but it is also getting more expensive to produce each successive unit. Proof of this trend can be seen in EROI (Exergy Return Over Investment) calculations and historical trends.

According to a new methodology proposed by Court and Fizaine [99], oil's peak EROI at 43:1, which occurred in 1943, will stand at 15:1 in 2018 and lower still at 10:1 in 2035. The same pattern can be seen for both gas and coal. The peak EROI for fossil fuels generally is 42.1, which is estimated to have occurred in 1965. This EROI will be down to 15:1 and 10:1 in 2060 and 2080 correspondingly.

Consequently, the alternative of fossil fuels with biomass, biofuels, biogas, and biopolymers is becoming an increasingly promising option. Remarkably, bioenergy is a renewable and relatively clean feedstock for creating modern energy carriers, such as electricity and transportation fuels [100].

Moreover, energy crops can recuperate, through photosynthetic processes, in their early life stages, the carbon dioxide emitted upon the burning of fossil fuels. This means they can create fuel alternatives within a short enough timeframe for the resource to be considered renewable.

Given that bio alternatives are created from plant or microbial sources, which use carbon dioxide as their feedstock in photosynthesis, an additional benefit is that the carbon cycle can be closed. Biomass can replace coal and biogas can replace natural gas. Biofuels can be exploited instead of oil, whereby the gasoline fraction is substituted for bioethanol, whilst diesel can be switched for biodiesel.

This chapter presents the calculation of the exergy consumed by Nature and society to produce 1 MJ of Bio-equivalent fuel to be stored as manmade replacement of the fossil fuel (Oil, Coal, and Natural Gas) which naturally produced by the ecosystem. The Exergy replacement cost of fuel will be calculated for the entire life cycle from solar radiation to fuel. “From Solar radiation to biomass” is the photosynthesis stage and “From Biomass to fuel” is the Bioproduction stage. After calculation of the exergy replacement cost of producing Bio-equivalent fuel, the Thermoeconomic environmental cost (TEEC) of producing electrical energy based on different technologies is calculated. Then, The Sustainability indicator is calculated based on the new proposed approach in comparison to other approaches that take ecological products and services in consideration.

An extensive literature review has been done in order to collect the required data to set up the case study. According to different cited analysis, the exergy efficiency of power block varies between 30% to 60% based on the used technology and fuel. The exergy efficiencies that have been taken within this study are 30%, 40%, and 55% for Diesel Engine, Coal power plant and Gas turbine, respectively [6].

There is a wide range of terrestrial plant photosynthetic exergy efficiencies. The value varies from anywhere between 2 and 41 percent [84–88], due to the considerable methodological differences that exist. Silva et al. [87] calculated the overall exergy efficiency of photosynthesis at 3.9 percent. They state that the exergy cost of photosynthesis is 25.44 MJ/MJ of glucose. In other words, for every 1 MJ of biomass produced, approximately 25 MJ of exergy is consumed. This exergy cost is the one taken as the baseline in the present case study.

The functional unit of our case studies is 1 MJ of bioproduct. To calculate the global ERC of a specific fossil fuel, not only the exergy cost of photosynthesis but also the exergy cost of Bio-equivalent production is needed to be known.

An Inventory of CExC of bioproducts derived from plant-based and waste, accounting for both renewable and non-renewable resources can be found in [93]. Values were standardised with MJ/MJ. Table [5] shows the average values of the total cumulative exergy consumption of bioproducts that they are included within the following case studies. The total cumulative exergy consumption is broken down to Renewable (RNW) and Non-renewable resources (NR) exergy consumption in one way and in the other way it is broken down to the exergy costs of Biomass, Water, Mineral, and energy.

5.1. Calculations

To produce 1 MJ (exergy) of Bio-alternative to compensate 1 MJ of fossil fuel that has been depleted from the natural stock,

The ERC of 1 MJ of Bioequivalent = The ERC of producing a Bio-alternative "from photosynthesis to fuel"

The ERC of producing a Bio-alternative = Cumulative exergy consumption of Photosynthesis + Cumulative exergy consumption of Bio-production

= {exergy cost of Biomass * exergy cost of photosynthesis} + {exergy cost of energy, water, and mineral}

Table 5 *Average Cumulative exergy consumption of Bioequivalents adapted from [93]*

Bioproduct	Average Cumulative Exergy Consumption (MJ/MJ)					
	Total		Subtotal			
	RNW	NR	energy	Biomass	Water	Mineral
Biochar	3.57	0.07	0.07	2.40	1.17	0.00
Biogas	0.16	2.84	0.13	0.54	2.33	0.00
Biodiesel	0.55	5.15	0.55	1.24	3.9	0.01

5.1.1. Case (A): Charcoal production

To produce 1 MJ (exergy) of Charcoal as a Bio-alternative to compensate 1 MJ of coal that has been depleted from the natural stock,

$$The\ ERC\ of\ producing\ a\ Bio-alternative$$

$$= \{25.44\ MJ/MJ\ *\ 2.4\ MJ/MJ\ \}\ +\ 1.17\ MJ/MJ\ +\ 0.07\ MJ/MJ$$

$$= 61.1\ MJ/MJ\ +\ 1.24\ MJ/MJ\ =\ 62.35\ MJ$$

The typical exergetic efficiency of Coal power plant is taken to be 40% which means if 1 MJ of coal is supplied as fuel, 0.4 MJ electrical energy would be produced. Which means according to the conventional CExC concept, the exergy cost of 0.4 MJ of electric energy generated from the coal power plant is 1 MJ (coal) only. But according to the new proposed concept

The TEEC of 0.4 MJ (electrical energy) = The CExC cost "in this case 1 MJ of coal as a natural resoucrs" + The ERC of producing a Bio-alternative "Charcoal in this case"

$$The\ TEEC\ of\ 0.4\ MJ\ (electrical\ energy) =\ 1\ MJ\ +\ 62.25\ MJ = 63.35\ MJ$$

And Hence,

$$The\ TEEC\ of\ 1\ MJ\ (electrical\ energy)\ produced\ from\ coal\ power\ plant = 158.37\ MJ$$

ignoring the consumption of all other natural resources within the power plant.

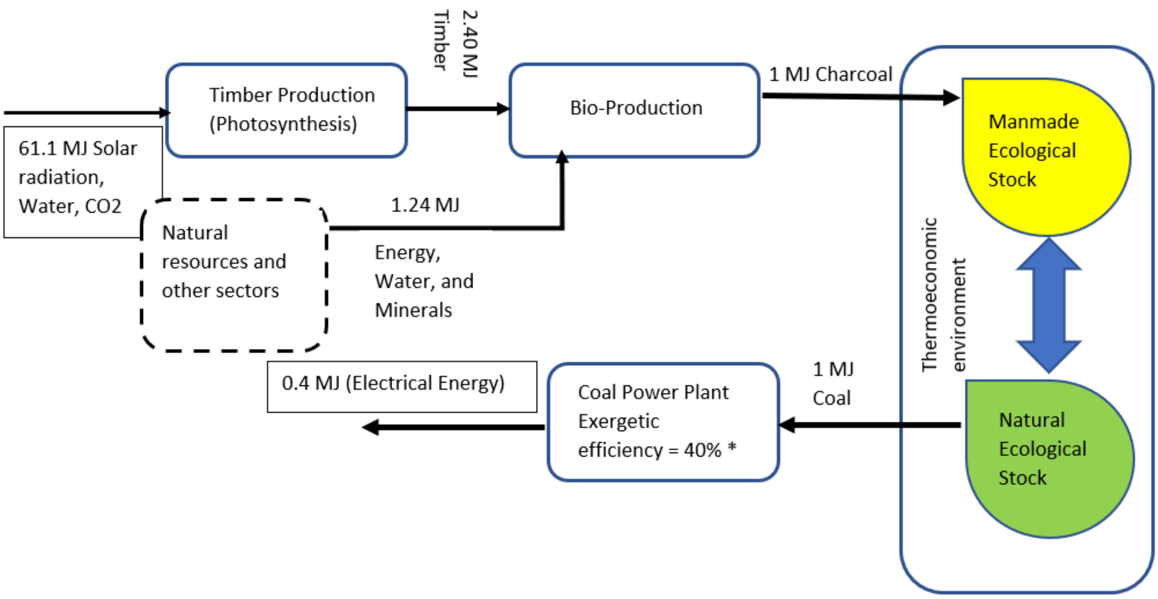

Figure 26 *ERC of Biochar*

5.1.2. Case (B): Biogas production

To produce 1 MJ (exergy) of Biodiesel as a Bio-alternative to compensate 1 MJ of biodiesel that has been depleted from the natural stock,

$$The\ ERC\ of\ producing\ a\ Bio-alternative$$

$$= \{25.44\ MJ/MJ\ *\ 0.54\ MJ/MJ\,\} + 2.33\ MJ/MJ\ +\ 0.13\ MJ/MJ$$

$$= 13.73\ MJ/MJ\ +\ 2.46\ MJ/MJ\ =\ 16.19\ MJ$$

The typical exergetic efficiency of Combined cycle power plant is taken to be 55% which means if 1 MJ of natural gas is supplied as fuel, 0.55 MJ electrical energy would be produced. Which means according to the conventional CExC concept, the exergy cost of 0.55 MJ of electric energy generated from the combined cycle power plant is 1 MJ (coal) only. But according to the new proposed concept The TEEC of 0.55 MJ (electrical energy) = The CExC cost “in this case 1 MJ of natural gas as a natural resource” + The ERC of producing a Bio-alternative “Biogas in this case”

$$The\ TEEC\ of\ 0.55MJ\ (electrical\ energy) =\ 1\ MJ\ +\ 16.19\ MJ = 17.19\ MJ$$

And hence,

$$The\ TEEC\ of\ 1\ MJ\ (electrical\ energy)\ produced\ from\ combined\ cycle\ power\ plant$$

$$= 31.25\ MJ$$

ignoring the consumption of all other natural resources within the power plant.

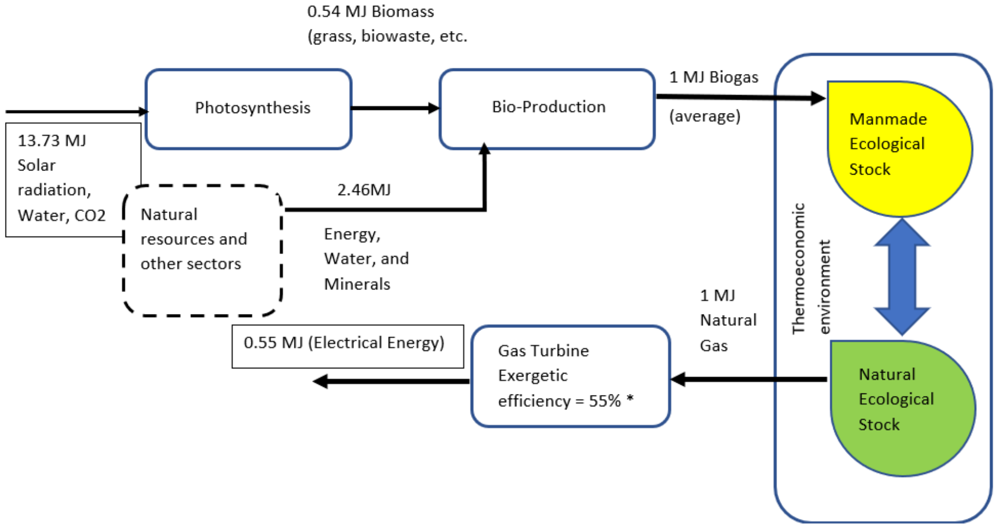

Figure 27 *ERC of Biogas*

5.1.3. Case (C): Biofuel production

The average decomposition of the products obtained from a barrel of oil corresponds to: gasoline 47%, diesel 23%, jet fuel 10%, liquefied petroleum gas (LPG) 4%, asphalt 3% and other products 13% [83]. Table [6] shows Oil Barrel breakdown for weighted ERC calculation and the geometric averages CExC value that has been calculated according to Eq. [63].

Table 6 *Oil Barrel breakdown for weighted ERC calculation adapted from [93]*

Oil Product	Barrel Share %	Bio-alternative	Bio-substitute CExC (MJ/MJ)	Biomass Fraction %
Gasoline	47	Bioethanol	6.93	29
Diesel	23	Biodiesel	5.70	21
Jet fuel	10	Biodiesel	5.70	21
LPG	4	SNG	2.24	35
Asphalt	3	Charcoal	3.64	66
Other products	13	Used Cooking Oil (UCO), Methanol, Biochar	6.05	27
Average			6.15	28

To produce 1 MJ (exergy) of Biofuel as a Bio-alternative to compensate 1 MJ of Oil that has been depleted from the natural stock, 43.06 MJ (exergy) of solar radiation, water and CO2 is needed in addition to other 4.46 MJ (exergy) of natural resources from other sectors. So, The ERC of 1MJ (Biofuel) equals to 47.52 MJ.

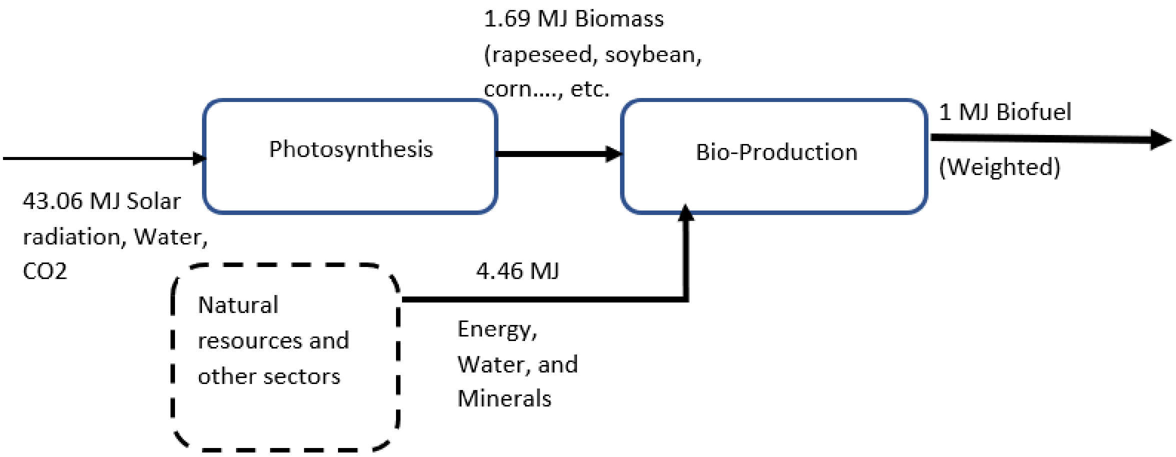

Figure 28 *ERC of Biofuel*

- ***Biodiesel Production***

To produce 1 MJ (exergy) of Biodiesel as a Bio-alternative to compensate 1 MJ of Natural gas that has been depleted from the natural stock,

$$The\ ERC\ of\ producing\ a\ Bio-alternative$$

$$= \left\{25.44\frac{MJ}{MJ} * 1.24\frac{MJ}{MJ}\right\} + 3.9\frac{MJ}{MJ} + 0.01\frac{MJ}{MJ} + 1.24\frac{MJ}{MJ}$$

$$= 31.6\ MJ/MJ + 4.46\ MJ/MJ = 36.06\ MJ$$

The typical exergetic efficiency of diesel engine is taken to be 30% which means if 1 MJ of diesel is supplied as fuel, 0.3 MJ electrical energy would be produced. Which means according to the conventional CExC concept, the exergy cost of 0.3 MJ of electric energy generated from the combined cycle power plant is 1 MJ (coal) only. But according to the new proposed concept

The TEEC of 0.3 MJ (electrical energy) = The CExC cost "in this case 1 MJ of diesel as a natural resource" + The ERC of producing a Bio-alternative "Biodiesel in this case"

$$The\ TEEC\ of\ 0.3\ MJ\ (electrical\ energy) = 1\ MJ + 36.06\ MJ = 37.06\ MJ$$

And hence,

$$The\ TEEC\ of\ 1\ MJ\ (electrical\ energy)\ produced\ from\ diesel\ engine = 123.53\ MJ$$

ignoring the consumption of all other natural resources within the power plant.

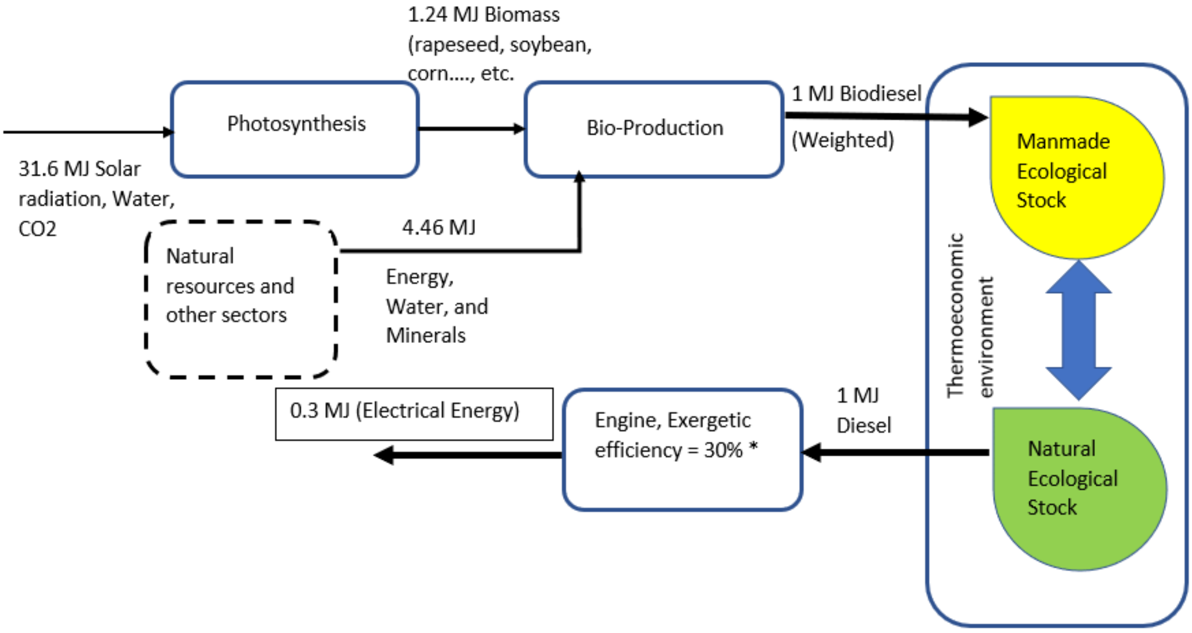

Figure 29 *ERC of Biodiesel*

5.2. Results

The exergy consumed by nature and society to produce 1 MJ equivalent of fuels which represents the exergy replacement cost (ERC) of 1 MJ of fossil fuel has been calculated and presented in Table [7]. The ERC of Oil conveys the weighted exergy cost of all the bioproducts that be consistent to the fraction that represent a barrel of Oil. The ERC of Natural gas is corresponding to the exergy cost of Biogas. Coal´s ERC is related to that of Biochar. ERC in GJ/Tonne of Fuel has been calculated, using the higher heating value (HHV) of each conventional fossil fuel. This value allows for a comparison between the 54 non-fuel minerals calculated by Valero and Valero in [90] with the fossil fuel calculations presented here. The HHVs of Coal, Oil, and natural gas has been taken as 22692 kJ/kg, 45664 kJ/kg, and 35533 kJ/kg respectively [6].

Table 7 *Fossil Fuel Exergy Replacement (ERC) and Thermoeconomic Exergy Cost (TEEC).*

Fuel Mineral	ERC (MJ/MJ_{Fuel})	ERC (GJ/Tonne)	C_{ex-P} ($MJ/MJ_{electricity}$)
Coal	62.35	1414.7	158.37
Oil	47.52	2170.0	-
Diesel	36.06	1646.64	123.53
Natural Gas	16.19	575.3	33
Phosphate Rock		0.4	
Gold		583668	

By using Eq. [69], The sustainability indicator of the system is calculated for each fuel respectively. The TEEC of the product (C_{ex-P}) of 1 MJ electricity based on the new approach for Coal, diesel, and natural Gas as fuels are 158.37 MJ, 123.53 MJ, and 33MJ accordingly. The exergy cost of product P, considering only RES C_{ex-RES} and the Exergy cost of the product P considering only Partially Renewable energy resources C_{ex-PRS} are neglected. The Exergy cost of the product P, considering only

NR resources (C_{ex-NRS}) in this case represents the exergy due to the HHV of the used conventional fossil fuel.

i_{ex-TEE}, as the ratio between the exergy cost, calculated ignoring the ERC of non-renewable resources and the Bio Stock replacement cost in the numerator and the total exergy TEEC (C_{ex-P}), calculated taking all terms into account, in the denominator.

Table 8 *TEE Sustainability indicator and ECDP of producing 1MJ of electricity*

Fuel Mineral	C_{ex-NRS} "Needed for 1 $MJ_{electricity}$" (MJ)	i_{ex-TEE} ($*10^{-3}$)	ECEC or M (Emergy) sej ($*10^{6}$) [a]	ECDP (Ecological Cumulative Degree of Perfection) $*10^{-3}$ J/sej [b]
Coal	2.5	15.75	144000	0.0069
Diesel	3.33	26.95	316350	0.0031
Natural Gas	1.81	54.84	124890	0.008

[a] Eq. [34] & [37] [b] Eq. [24]

The sustainability indicator when using Natural Gas as Fuel, has the highest value with (.0548). This is a rational value due to the higher exergetic efficiency of gas turbine and the lower value of Natural Gas ERC. This low value of ERC of natural gas because its Bioequivalent can be derived from waste and hence, the exergy consumed prior to disposal was assigned to the Crop´s primary use. The i_{ex-TEE} when using coal as fuel, is the lowest values with ($15.75*10^{-3}$) despite of Coal power plant ´exergetic efficiency is not being the lowest among studied technologies. But, because of its high ERC in comparison to its intrinsic exergy value (HHV). High ERC is due to the higher exergy consumption within Biomass production stage as it represents almost 65% of the total exergy consumption for Bioequivalent fuel production. The new methodology is consistent with the ECEC methodology. Both are demonstrating the same fact that the methodologies that are being used now to evaluate a system's sustainability, are underestimating the real exergy cost of depleting the natural stock of fossil fuel as shown in Table [8].

Fig. [30] represents the natural resource consumed in the bioproduction processes into four categories. Biodiesel has the highest exergy cost related to bioproduction stage due to a high proportion of its exergy cost linked water, this is not because of irrigation but rather the washing process of biodiesel [83].

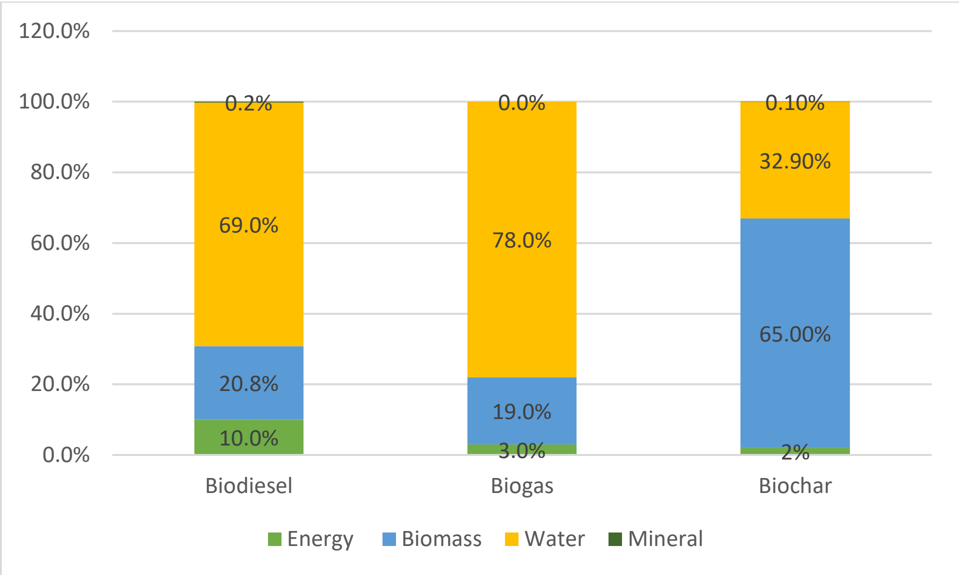

Figure 30 *Resource contributions to the exergy cost of Bioproducts (from Crop to fuel)*

In comparison to the world mineral depletion evaluated by Valero and Valero [90]. The total depleted amount was 5.15 * 10^5 Mtoe where the nonfuel minerals represent 20.38 % of the total ERC. Fuel mineral, using the higher heating value (HHV), represents 79.62 %. Table [9] shows that Valero approach, compared to our new approach, sub-estimated the ERC by more than forty-fold on average (calculated by dividing total ERC based on our approach to Valero´ ERC). The ERC of non-fuel minerals, based on our approach, represents only 0.54% of the new total (1.92*10^7 Mtoe) as shown in Fig. [31].

Table 9 *ERC values of Minerals (fuel and non-fuel) based on Valero approach and new TEE suggested approach*

	ERC (Mtoe)				
	Non-fuels minerals	*Coal*	*Oil*	*Nat. Gas*	*Total*
Valero and Valero	105,000	155,000	172,000	83,200	515,200
New approach of TEE	105,000	9,640,000	8,190,000	1,350,000	19,285,000

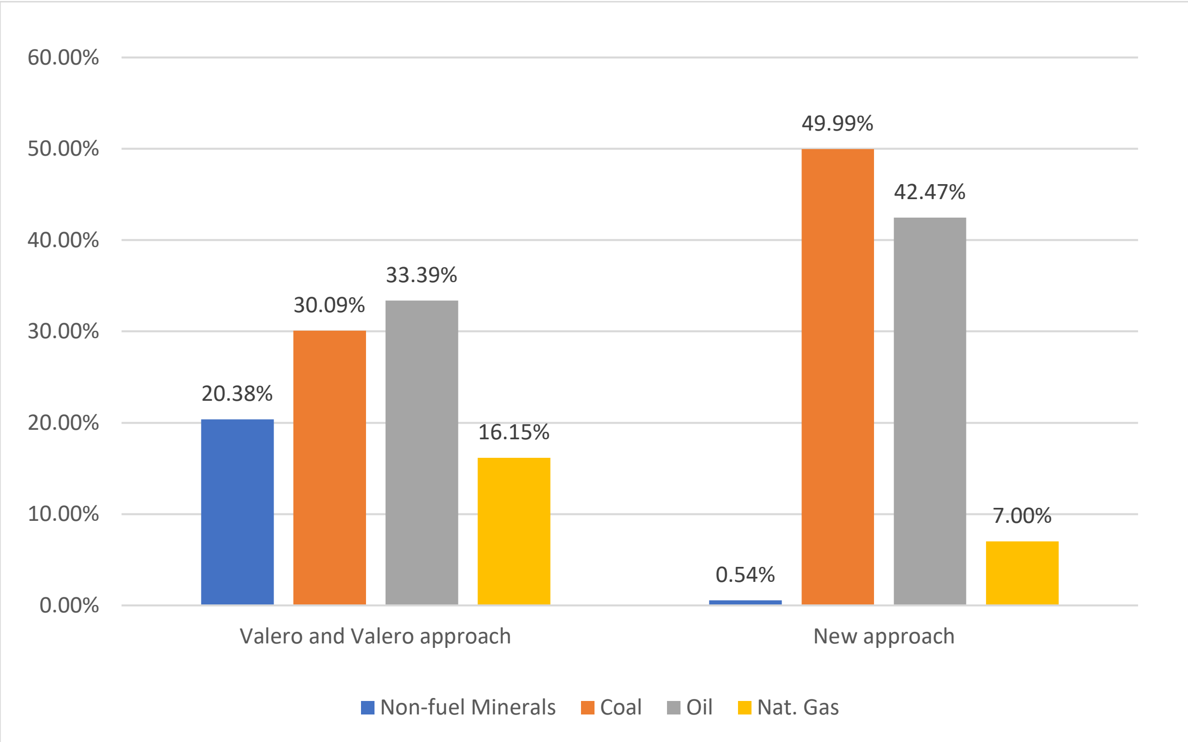

Figure 31 *Comparison between the New approach and Valero approach (Estimation of Depletion of minerals in terms of ERC)*

6. Discussion

As an indicator to amount the sustainability of resource depletion, the TEEC states the physical and economic costs of making a fuel and non-fuel resource available to society, not just from a natural deposit, but from our waste streams and our Earth's sinks (landfills, atmosphere, and polluted oceans), relative to a depleted.

The new methodology is consistent with the ECEC methodology. Both are demonstrating the same fact that the methodologies that are being used now to evaluate a system's sustainability, are underestimating the real exergy cost of depleting the natural stock of fossil fuel. What gives the advantages for the new proposed methodology over the emergy concept, or the ecological cumulative exergy consumption methodology is that the latter have a lot of uncertainties and are trying to simulate the ecological processes that happened millions of years ago. Bio-Stock replacement cost is a concept of creating a Bio-alternative using the best available technology at the present which is applicable and there are many plants producing different kinds of Biofuel. This makes the new approach less uncertain despite the lack of a lot of data that would help make the approach results more precise.

The original ERC methodology expressed the ERC as the cost that the current generation would have to pay in order to reverse the mining effectively place a mineral back into its original deposit, using current best available technology. Nevertheless, this is not the cost current generations should pay to make sure that future generations have access to resources. Because first, if we are trying to preserve geological/mineral inheritance, the chemical composition of a resource is irrelevant to a deep discussion on sustainability. Current generations do not have to fulfil the sustainable development requirements by supplying future generations with oil. Oil is only as valuable as the services that it delivers. Current generations shall leave future generation with at least the same quality of life they must eventually leave them with a healthy natural environment along with the technological developments and the technical capabilities required to attain a resource that enables them to experience the benefits enjoyed today because of fossil fuels. Second, there is no benefit to locating oil back into a deposit as society neither wants nor needs to return oil to its original geological formation. Rather society requires easy access to oil in a useable deposit. Third, there is no reason to overturn the mining and beneficiation process, for reasons linked to the second point and as the case of biofuels reveals. These reasons support the need to reform the ERC concept so that it looks at the services that material delivers, rather than the material themselves.

Using biofuels to make an alternate pathway within the TEEC concept forces a paradigm shift towards looking at function. If TEEC is a measure of sustainability, and an indicator to be used by politicians and industry to take hard line decisions, it is important that sustainability is seen in those terms. The TEEC has an important contribution because, by calculating the replacement cost, it is asking society to take a cautious approach to extraction, to minimise material use and close energy and material cycles, in a way that provides future generations with the resources they need to flourish. Using this new method, we found that using the HHV as a proxy caused, on average, a forty-fold sub-estimation of the physical cost of fossil fuel depletion when considering solar radiation to fuel.

This thesis is not stating that fossil fuel burning and any subsequent replacement with biological equivalents is a sustainable or desirable end point. The use of biomass and biofuels, particularly, is already associated to notable drawbacks and uncertainties [101]. These include risks to biodiversity, water scarcity and pollution and the utilisation of fertile soils currently sustaining food production [102–104]. And as the World Resources Institute points out, even if all the world's harvested biomass were used for energy, this would deliver just 20 percent of the world's energy needs in 2050 [105]. In other words, there is not enough fertile land to maintain current energy demand, and even if only five percent were met there would be severe implications on food production and societal equity. This is just one of the ethical issues surrounding first, and some second generation, biomass and biofuels that are already being raised and discussed in the mainstream media and at policy level [106].

7. Conclusion

Exergy cost accounting presents the sum of direct and indirect exergy consumption, as a measure of resources required for obtaining a certain product. The necessary definition of a proper ultimate boundary of the exergy cost accounting may be carried out by introducing the TEE, consistently to assess the sustainability of the production of goods and services. Then, the exergy replacement cost of mineral resources, proposed by Valero and Valero, may be introduced as a meaningful progress of aactual Exergy cost accounting methodologies, consistently with the frame of the TEE.

In the same way, also the proposal by Rocco and Colombo for a definition of the exergy values of labour and capital (directly derived from the input/output algebra by Leontief) is shown to be also consistent with the framework of the TEE and can therefore be used for evaluating the Exergy equivalent of capital and human work. In this way, the production factors, like capital investment, human labor, and environmental resources, can be unified into a common exergetic description.

To properly consider also the interaction of the production system with the biological processes, the bioresource stock replacement cost is here introduced, taking advantage of the idea of partially renewable resources (the living biomass) contained inside the TEE. Given using exergy cost accounting for assessing the sustainability of a specific product, or service, it is important to notice that the TEE framework allows us to assess the impact of polluting emissions based on the actual exergy stock depletion throughout the TEE. It can be explained how virtuous plants, which effectively include the emission neutralization system, may have a specific exergy cost lower than polluting plants, therefore justifying the adoption of devices for strongly reducing the polluting emissions from an exergy cost accounting point of view.

The “Bio-stock replacement cost” approach highlights the cost of re-capturing and re-concentrating a resource that has been depleted and dispersed by anthropogenic activity. It was originally only applied to non-fuel minerals because of the belief that to calculate a fuel’s ERC one would need to re transform the carbon dioxide emitted, on fossil fuel combustion, back into a fuel of the same chemical composition. This then led to fossil fuels either being ignored within the ERC calculation or a fuel’s

HHV being used as a proxy, which is not a consistent method. In this thesis, we pursued to rectify the theoretical tensions present in the ERC theory by reframing the depletion problem and regulating the methodological steps and calculations for both fuel and non-fuel minerals. Under the assumption that planting fuel crops joint with bio-energy production is the best technology available, we presented how the "Bio-stock replacement cost" approach may be used to estimate the cost of closing the carbon loop, via photosynthetic capture of atmospheric CO2 and its conversion into a biomass, which can then be directly burnt or converted into a different form, such as biofuel. The usage of, say biofuels, as a measure of a fuel's ERC instead of other technologies (such as solar panels) tied the cradle to grave LCA to the grave to cradle ERC. Moreover, the resulting LCA boundary extension "from solar radiation to fuel" took into consideration a huge exergy source that had been previously ignored. The new method also delivers a paradigm shift towards an ERC approach emphasize on function instead of chemical composition. The idea of sustaining a chemical composition is not appropriate and is a superfluous barrier to the further development of the ERC calculation and its role in forming environmental debates.

In addition, an exergy-based sustainability indicator easily arises as the ratio of the exergy cost, calculated neglecting the exergy replacement cost of non-RES and the bioresource stock replacement cost, and the total bioresource stock replacement exergy Thermoeconomic Environment cost, calculated taking all terms into account. The new exergy-based sustainability indicator is expected to be well-suited for expressing the resource sustainability of goods and services. It is equal to one in the ideal case where all direct and indirect consumptions are in form of RES, allowing a clear perception about how far the process at hand is from the ideal case, and which is the margin of the possible improvement.

Finally, it allows us to highlight the advantage of recycling and the usage of non-rare mineral resources, because they both reduce the exergy replacement cost of non-RES and the bioresource stock replacement cost of partial RES. In the same way, the disadvantage of consuming rare mineral or biological resources.

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