The duality between exergy efficiencies and exergy costs. The Structural Theory and the Relative Free Energy function.

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#### **Motivation**

- Costing is one of the most important applications of exergy. Exergy allows more precise allocations than energy or even money when two or more stream bifurcations appear in energy systems.
- Exergy cost analysis has become a complementary analysis of energy systems. However, such analyses strongly depend on the practitioner expertise.
- A number of "reasonable" decisions need to be taken to get fair results.
- This paper focus on describing a mathematical theory that support such decisions but also to analyze the pitfalls or weaknesses of conventional exergy costing"



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#### Introduction

- The "exergy cost", (kWh)(Valero e al, 1986) has been otherwise named "cumulative exergy consumption" by J. Szargut, (1986) or "embodied exergy" by some authors.
- It measures the amount of exergy needed to manufacture a product when the boundaries of the production plant, a disaggregation level, and the exergy efficiency of each and every component have been defined.
- The exergy of a stream measures what can be done with respect to a given environment and,
- the exergy cost measures how many irreversibilities happened to manufacture a product. It's like the "exergy backpack" or its "exergy footprint" of a stream, i.e. the "past" characterization (history) of the stream.



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### Introduction

- Which "reasonable" decisions need to be taken to get fair results?
- These are: Disaggregation level, definition of exergy efficiencies, reference environment for exergy calculations, the origin of wastes formation and some others.
- These decisions define the "Productive Structure".

$$Ex_{int} - Ex_{out} = Irreversibility \rightarrow F - P = R + I_{int} = I_{total} \geq 0$$

The exergy efficiency of each component is defined as :

$$\eta = \mathbf{P} / \mathbf{F}$$
 or its inverse  $\kappa = \mathbf{1} / \eta = \mathbf{F} / \mathbf{P}$ 

the unit consumption of resources to produce  ${m P}$  ,

with  $\kappa > 1$ , or  $0 < \eta < 1$ 

We define *unit exergy cost* κ\* as the amount of resources needed to manufacture a product divided by its exergy



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#### Introduction

- Rule P, if two products are produced in the same place and have the same quality, it is logical that we allocate the production costs in proportion to the quantity of each one of them.
- Rule F, if a resource is not exhausted and leaves the process, then it is logical that each unit of exergy of the resource, would have the same unit cost.





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The physical behavior of the plant does not depends on the analyst choice.

- "reasonable" decisions are not enough!
- Why exergy? one is always in doubt which function to be used for describing the plant. Energy, Exergy, Free Energy (Gibbs) function, or any other generic function?
- We need a General Theory supporting such decisions and capable of analyzing the pitfalls or weaknesses of conventional exergy costing.



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- Suppose any energy system that consumes resources and manufactures products that can be characterized by a thermodynamic function *E* of the generic type, *E* = *m* (*h*-*T<sub>x</sub> s*)
- ✤ Note that when T<sub>x</sub>, is zero the function E is the enthalpy, when T<sub>x</sub> is the ambient temperature, E becomes the exergy, and if T<sub>x</sub>, is the temperature of the system E will be the Gibbs function.
- The physical behavior of the plant does not depend on the analyst choice.
- One is always in doubt which function to be used for describing the plant. Energy, Exergy, Free Energy (Gibbs) function, or any other generic function?



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 We can describe the mathematical behavior of each component through functions of the type

$$E_i = f_i(\{x\}, E_j)$$

Where i = 1 ... number of component inputs and j = 1 ... number of component outputs. While {x} is the set of internal parameters that govern it.



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- Such type of function, can be developed into a Taylor series.
   When sufficiently small linear intervals of behavior are chosen it is always possible to reject second order terms.
- Then, the approximate characteristic equation for each component will be:

 $E_i = k_{i1}E_1 + k_{i2}E_2 + \dots$ 

Where k<sub>ij</sub> are the unit consumptions of resource i to produce product j.

$$k_{ij} = \left(\frac{\partial E_i}{\partial E_j}\right)_{(E_n,k_{in}) \text{ constant}} \text{ or } E_i = \sum_{j=1}^{\infty} \left(\frac{\partial E_i}{\partial E_j}\right) E_j \qquad i = 1...v_e = n^{\circ} \text{ of inputs to component "I"} \\ v_g = n^{\circ} \text{ of ouputs from component "I"}$$

\* In the I-O theory by Leontieff, they are named " technical production coefficients"



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On the other hand, the globally considered plant will receive some resources, be these E<sub>o</sub>. If we identify the unit cost with the derivative:

$$k_i^* = \left(\frac{\partial E_0}{\partial E_i}\right)_{ceteris \ paribus}$$

It is mathematically evident that for each and every component it fulfills:

$$\left(\frac{\partial E_0}{\partial E_j}\right) = \left(\frac{\partial E_i}{\partial E_j}\right) \left(\frac{\partial E_0}{\partial E_i}\right)$$

 $k_i = k_{ii} k_i$ 

Or



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- The application of this equation allows to explain, as particular cases, the *F* and *P* rules.
- As an example, suppose a turbine where its efficiency should coincide with its characteristic equation, then:

$$\eta = \frac{P}{F} = \frac{Ex_3}{Ex_1 - Ex_2} \equiv 1/k \text{ or } Ex_1 = Ex_2 + k Ex_3$$

It is mathematically evident that for such component it fulfills the
 F rule :

$$k_3^* = k k_1^*$$
 and  $k_2^* = k_1^*$ ,



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On the other hand, if we consider a typical electric power distribution system, and *its efficiency were its characteristic equation*, then:

$$\eta = \frac{P}{F} = \frac{Ex_2 + Ex_3}{Ex_1} \equiv 1/k \quad \text{or} \quad Ex_1 = k Ex_1 + k Ex_2$$

It is mathematically evident that for such component it fulfills the
 *P* rule :

$$k_{2}^{*} = k k_{1}^{*}$$
 and  $k_{3}^{*} = k k_{1}^{*}$  or  $k_{2}^{*} = k_{3}^{*}$ 



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More in general, suppose a process like the one in the following figure:





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Its disaggregation allows proposing the following linear equations:

 $E_0 = k_{01} E_1 + k_{02} E_2$  $E_1 = k_{13} E_3 + k_{15} E_5$  $E_2 = k_{24} E_4$ or  $E_3 = const.$  $E_3 = \omega_3 (const.)$  $E_4 = \omega_4$  (const.)  $E_A = const.$  $E_5 =$  $E_s = k_{sd} E_d$ 



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Then, by the rule of the chain of derivation allows to write that:

| $\frac{\partial E_0}{\partial E_0} = I$   | or | $k_0^* = I$                                |
|---|----|--|
| $\frac{\partial E_0}{\partial E_I} = \frac{\partial E_0}{\partial E_I} \frac{\partial E_0}{\partial E_0}$   |    | $k_{I}^{*} = k_{0I} k_{0}^{*}$             |
| $\frac{\partial E_0}{\partial E_2} = \frac{\partial E_0}{\partial E_2} \frac{\partial E_0}{\partial E_0}$   |    | $k_2^* = k_{02} k_0^*$                     |
| $\frac{\partial E_0}{\partial E_3} = \frac{\partial E_1}{\partial E_3} \frac{\partial E_0}{\partial E_1}$   |    | $k_3^* = k_{I3} k_I^*$                     |
| $\frac{\partial E_0}{\partial E_4} = \frac{\partial E_2}{\partial E_4} \frac{\partial E_0}{\partial E_2} + \frac{\partial E_5}{\partial E_4} \frac{\partial E_0}{\partial E_5}$ |    | $k_4^* = k_{24} k_2^* + k_{54} k_5^*$      |
| $\frac{\partial E_0}{\partial E_5} = \frac{\partial E_1}{\partial E_5} \frac{\partial E_0}{\partial E_1}$   |    | $k_{5}^{\bullet} = k_{15} k_{1}^{\bullet}$ |



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It can be observed that the matrix of unit consumptions (K) is common and is transposed <sup>t</sup>(K) between both equations :

$$\begin{bmatrix} k^{*} \\ k^{*} \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ k_{01} & 0 & 0 & 0 & 0 & 0 & 0 \\ k_{02} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & k_{13} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & k_{24} & 0 & 0 & k_{54} \\ 0 & k_{15} & 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} 1 \\ k^{*} \\ 1 \\ k^{*} \end{bmatrix} + \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}$$

or  $K^* = (K) K^* + K^*_0$ 

 $E=(K)E+\Omega$ 

The first equation is called primal of the structure and the second is called its dual.



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or

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- Every productive structure or linear interpretation of a system takes a primal representation to which corresponds a single dual and vice versa.
- While the arrows in the productive process point from the resources towards the products, the costs -or dual- point from the products towards the resources.



#### Costs seek the origin, the products seek its destiny!



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Note also that for each subsystem it is fulfilled that:

(1) 
$$k_0^* E_0 = k_1^* E_1 + k_2^* E_2$$
  
(2)  $k_1^* E_1 = k_3^* E_3 + k_5^* E_5$   
(3)  $k_2^* E_2 + k_5^* E_5 = k_4^* E_4$ 
or
$$\begin{bmatrix} E_0^* = E_1^* + E_2^* \\ E_1^* = E_3^* + E_5^* \\ E_2^* + E_5^* = E_4^* \end{bmatrix}$$



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Now, we can define the *plant's incidence matrix* whose *a<sub>ij</sub>* elements are "1" if the stream *j* enters subsystem *i*, "-1" if it exits, and "0" if they do not interact, then for the analyzed case:

$$A = \begin{bmatrix} +1 & -1 & -1 & 0 & 0 & 0 \\ 0 & +1 & 0 & -1 & 0 & -1 \\ 0 & 0 & +1 & 0 & -1 & +1 \end{bmatrix}$$

in general

 $AE^*=0$ 

This is the cost conservation equation. Costs of the inputs of any component are transferred entirely among all the outputs.



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Equilibrium Thermodynamics for open systems can simply be summarized in the following equations:

| Mass Balance     | : AM = 0  |
|------------------|-----------|
| Enthalpy Balance | : AH = 0  |
| Exergy Balance   | : AEx = I |
| Ex.Costs Balance | : AEx*= 0 |

where, *M*, *H*, *Ex* are vectors whose elements are mass, enthalpy and exergy of the material streams: *m<sub>i</sub>*, *m<sub>i</sub> h<sub>i</sub> and m<sub>i</sub>*(*h<sub>i</sub>* - *T<sub>o</sub> s<sub>i</sub>*); *zero*, *Q* and *Q* (1- *T<sub>o</sub>*/*T*) if they are heat flows; and *zero*, *W*, and *W*, if they are working flows, respectively



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### **Doubts with Exergy**

- It is not convenient to mythologize exergy. So why not thinking beyond it?
- The exergy and its corresponding exergy cost depend on T<sub>o</sub> which has been arbitrarily (but reasonably) selected.
- If we use the cost to measure the impact on resources due to malfunctions (or component's degradation), the result must be independent on arbitrary selected parameters.
- It would be interesting to see the amount of resources needed to compensate a degradation of any component at constant production.
- Because one way of understanding the Second Law is relating degradation to the amount of resources consumed.



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Before generalizing the problem, it is convenient to see a simple case like that of a turbine whose expanding flow produces a work on the axis. In an (h, s) a diagram the actual process evolves



If the quality of the steam, 1, is constant, and the turbine degrades but keeps its the same production, an increase in the generation of entropy will result in an increase of the amount of steam, 1, entering the turbine.



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- Suppose that as a consequence of the degradation the new state of the outstream is 2' characterized by (h<sub>2'</sub>, s<sub>2</sub>)
- Differential analysis under these conditions leads to

W = const. $(h_2 - h_1) dm = mdh_2$  $h_{1'} s_1 = const.$  $(s_2 - s_1) dm + mds_2 = dS_g$ and defining

$$T_{d_2} \equiv dh_2/ds_2$$

we get





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# **Doubts with Exergy**

That is, an <u>exact mathematical expression</u> of the relationship that exists between local degradation and the increase of associated resources.

$$\left(\frac{dm}{dS_g}\right)_{\substack{degrad.\\path}} \frac{T_{d_2}}{(h_1 - h_2) - T_{d_2}(s_1 - s_2)}$$

- It was obtained by A. Valero (1992) and the function (h<sub>1</sub>-h<sub>2</sub>)-T<sub>d</sub>(s<sub>1</sub>-s<sub>2</sub>)
- It was called "relative free energy", while E. Sciubba proposed calling T<sub>d</sub> as "dissipation temperature".
- Royo et al. in 1994 and 1995, extensively developed its properties.



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#### The h-s deterioration(s) path(s) of energy systems

- Given a deterioration cause, r, of an energy component, either intrinsic or induced, we can identify a geometric path in the plane (h, s) of the possible exit flow states.
- Let h<sub>2'</sub>=h<sub>2'</sub> (s<sub>2'</sub>, r) the function describing this dissipation path of the exiting stream
- $1 \rightarrow 2$ : design path of the stream in the component
- 1  $\rightarrow$  2': stream path after component's deterioration
- $2 \rightarrow 2'$ : dissipation path of the exiting stream:  $h_{2'}=h_{2'}(s_{2''}, r)$





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#### The h-s deterioration(s) path(s) of energy systems

- \* if the intercept in the **h-axis** of the tangent line is  $\ell$  and has a slope  $T_d$ ,
- \*  $T_d = (h \ell)/(s 0)$ , or  $\ell = h T_d s$  i.e.  $\ell = \ell (T_d)$





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#### The h-s deterioration(s) path(s) of energy systems

- This equation :  $\ell = \ell (T_d)$  is the Legendre transform of the deterioration path,  $h_{2'}=h_{2'}(s_{2'}, r)$ .
- In fact, having pairs of  $(I_{2'}, T_{d,2'})$  for each exit state, 2', of the \* component provide the same information as pairs  $(h_{2'}s_{2'})$ .





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### **Doubts with Exergy**

✤ It can be demonstrated that

\* 
$$(dm / dS_g)_r = T_0 / [(h_{2'} - h_2) - T_0 (s_{2'} - s_2)]$$
  
=  $T_d / [(h_1 - h_2) - T_d (s_1 - s_2)]$ 

This expression relates T<sub>o</sub> with T<sub>d</sub>, and can be used to relate irreversibilities with the **Relative free energy** too.



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In general, it can be shown that a relationship between the increase in entropy degradation in a process and the amount of additional resource q<sub>l</sub> required under the specifications already explained:

$$\frac{\partial q_{\ell}}{\partial S_g} = \frac{T_d}{\ell}$$

- This expression shows that the Second Law has not yet said the last word in the relationship between quantity, quality, cost and irreversibility.
- Perhaps we will see a broader development of the theory here sketched



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To what extent the linear characteristic equation

 $E_i = k_{i1}E_1 + k_{i2}E_2 + \dots$ 

of a component can be conformed to

its efficiency definition, *F* – *k P* = **0**?

In fact, exergy efficiency must be coherent with the

component's design purpose, but one designs machines

by observing the behavior of nature.

- So what is first, efficiency or nature?
- We obtained that why the F and P propositions, and any other proposal may be rational or not under a given disaggregation scheme.



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- Why the "exergy cost" of any stream in a physical structure is the mathematical dual of the "exergy" of such a stream, and vice versa,
- The exergy cost and the exergy are like specular images of the same entity.
- We have seen which "reasonable decisions" of the Exergy Cost Theory are correct or not.
- Are exergy costs natural costs?



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- A compact vision of current day Technical Thermodynamics/Thermoeconomics under
  - Mass Balance : **AM** = **0**
  - Energy Balance : **AH** = **0**
  - Exergy Balance : **AEx** = **I**
  - Exergy Costs Balance : **AEx\* = 0**



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- A costing theory applicable to any thermodynamic function like, Enthalpy, Exergy, Gibbs Free Energy or any other.
- In analyzing this last point, we found a new Thermodynamic function, called the *Relative Free Energy*, *l*, defined as

$$\ell = (h_1 - h_2) - T_d(s_1 - s_2)$$

Where T<sub>d</sub> is the "dissipation temperature" of a given deterioration path of a process component.



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✤ Also we have demonstrated the equation

$$(dm / dS_g)_r = T_d / [(h_1 - h_2) - T_d (s_1 - s_2)]$$

And its relationship with the exiting exergy stream

$$(dm / dS_g)_r = T_d / [(h_1 - h_2) - T_d (s_1 - s_2)] = T_0 / [(h_{2'} - h_2) - T_0 (s_{2'} - s_2)]$$



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- \* The Legendre transform of the deterioration path,  $h_2 = h_2 (s_2, r)$ is the relationship  $l_2 = l_2 (T_{d,2}, r)$ .
- In other words, the pairs l r and T<sub>d,r</sub>, are so inseparable in a deterioration path, r, as the pairs h<sub>r</sub> and s<sub>r</sub> do.
- ✤ As demonstrated by Royo et al. (1994) the general formula is

 $(dq / dS_g)_r = T_d / (\ell_1 - \ell_2)$ 

where q means a general quantity, including mass, heat or work for different technical equipment under a given deterioration path.



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- This theory opens new fields of knowledge, since new questions appear:
- Is exergy the best thermodynamic function when diagnosing systems? Why T<sub>0</sub> needs to be the same for each component of a given structure?
- Can we use this theory to assess objective average costs free from assumptions? Marginal costs are related with behavior while exergy costs with history. Do exergy costs may be related with expected behavior?



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- Or in other words, is expected behavior a way of selecting the best efficiency definition of any equipment?
- All these ideas are tools for future developments, even if they were described by our research group in the nineties. (Valero, 2000).
- If cost is a measure of expended resources to produce something, then, costing with the Relative Free Energy instead of Exergy would open a new field of a more precise theory of Thermoeconomics.



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### Thank you very much for your attention!



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