Comments on the Paper
'A Brief Commented History of Exergy from the Beginnings to 2004'

E. Sciubba and G. Wall
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and Authors' Response

The paper by E. Sciubba and G. Wall (Reference [1]) contains several errors, inaccuracies, and omissions. In the following, I will only address a few:

1. Equation 1 in Reference [1] (page 4) does not represent the specific exergy of an open system ***S*** at thermodynamic state 1, as the authors mention, but only the specific exergy associated with a stream of matter. The specific *physical* exergy (e_{sys}^{PH}) of a system, regardless of whether it is an open or closed system, is given by [2,3]

$$e_{sys}^{PH} = (u_1 - u_0) + p_0(v_1 - v_0) - T_0(s_1 - s_0) \tag{1}$$

and not, as given in [1], by

$$e^{PH} = (h_1 - h_0) - T_0(s_1 - s_0), \tag{2}$$

which represents the specific physical exergy of a **material stream**.

In the same way, the following equation (Equation 2 in Reference [1])

$$\begin{aligned} e_1 - e_2 = h_1 - h_2 + \frac{V_1^2 - V_2^2}{2} + g(z_1 - z_2) + \\ + \Delta g_{1,0} - \Delta g_{2,0} + RT_0 \ln\left(\frac{c_1}{c_2}\right) - T_0(s_1 - s_2) \end{aligned} \tag{3}$$

refers to a material stream and not to an open system [1] undergoing a process from state 1 to state 2. A distinction between a system and a material stream (entering or exiting an open system) should be made in an exergy analysis.

2. Contrary to statement b) on page 4 of Reference [1], *the exergy of a system is always positive, whereas the exergy of a material stream could become negative only when the pressure p of the stream is lower than the pressure p_0 of the reference environment*. In this respect, splitting the physical exergy of a material stream into thermal and mechanical exergy [4] helps to clarify the issue, because all exergy forms of a material stream but the mechanical exergy are always positive and the mechanical exergy becomes negative only when $p<p_0$. When the case is so clear, there is no need to confuse the reader by saying that "There may be particular combinations of the values of the thermodynamic parameters such that [the total specific exergy of a system becomes negative] $e_1<0$" (page 4 in [1]).

3. It is not always true that "chemical energy cannot be entirely transformed into – say- mechanical work" (page 3 in [1]). This statement applies mainly to gases. The chemical exergy of pure carbon (C), for example, is higher than its chemical energy (heating value), which shows that the mechanical work obtainable from carbon through a reversible process taking place at the conditions of the reference environment is higher than its chemical energy. Similar conclusions are drawn when we compare the higher heating value (chemical energy) of a coal with its exergy value (potential to generate mechanical work), the latter being larger than the former. Finally, the chemical exergy of a liquid fuel is smaller than but relatively close to the higher heating value of the fuel.

4. With respect to exergetic efficiency, the reader is left with the impression, that the three equations 5, 6, and 7 presented prominently in [1] are acceptable and perhaps the only ones available for evaluating the performance of components or systems. However, these efficiencies could mislead because they use the concept of "exergy input" instead of the more appropriate concept of the "exergy of fuel". The general concept of "product" and "fuel" introduced by me in References [5] and [6], used by many researchers since then (including Valero and co-workers starting with [7]), and finalized in [8,9] is not mentioned at all in Reference [1]. This, however, is, not only in my opinion, the most advanced and objective concept in dealing with questions related to the efficiency of energy conversion processes and systems.

5. The term *energy* does not mean literally "internal work" in Greek, as mentioned on page 6 [1], but "*contains in it the capability to conduct work*". Thus, the literal meaning of *energy* is very close to the concept of *exergy*. Furthermore, Rant used the prefix *ex* in exergy, not to "imply an external quantity" (page 6 in [1]), but to denote the *capability for work extraction*.
6. The term *exergoeconomics* was coined by me [5] in 1984, to indicate a particular combination of an exergy analysis with an economic analysis, in which combination the *exergy costing principle* is applied. For any other combination of a thermodynamic analysis with an economic analysis the broader term *thermoeconomics* should be used. It is apparent that the authors of [1] ignore these facts when they write "… Thermo-Economics (so strongly linked to exergy to be sometimes called Exergo-Economics)…" (page 2 in [1]), and "the joint application of exergy analysis and engineering economics was proposed, under the name of Exergo-Economics (in Europe, Rabek 1964, Szargut & Petela 1964, Baehr et al 1965, Brodyanski 1965…" (page 18 in [1]). Needless to say that none of the above authors (as a matter of fact nobody before 1984) has ever used the term *exergoeconomics* to characterize their own work or the work by others. Some things become more evident, if we consider the fact that both Szargut and Baehr have repeatedly expressed their opposition to the concept of exergoeconomics (that means to exergy costing) or thermoeconomics, as it was called at that time.
7. The presentation of section 8 "Thermo-Economics" in [1] demonstrates a low level of knowledge and understanding by the authors. Here I will mention only one historical point since the article deals with the history of exergy. On page 19 in [1] the authors write "The present formalization of the theory and applications of Thermo-Economics is due entirely (the underlining is mine) to Valero and co-workers, who in the above quoted publications provided not only a solid theoretical foundation, but also opened the way to a series of important applications to process and system analysis. A formally slightly different method was proposed by Szargut (1971, 1986), Tsatsaronis (1990), Tsatsaronis & Krane (1992), but in essence their approach is embedded in Valero's formulation" (my underlining again).

   For the sake of historical truth, we must put things in the right perspective: The general concepts of "fuel" and "product" (in conjunction with exergy analysis and exergoeconomics), "cost per unit of exergy of fuel and product", "cost of exergy destruction" as well as the general formulation of exergy balances and cost balances were developed by me [5,6,10,11] in the time period 1983-1985.

   Valero and Lozano, who were familiar with my work, used a *special case* of these developments (the case in which the contributions of investment costs and operating & maintenance expenses are neglected in the cost balances) to present the "exergetic cost theory" [7,12]. In this theory, the additions (both very useful) to my developments were (a) the division of the variables by the cost of the fuel to the total system, and (b) the matrix formulation. The fact that Valero and co-workers did not mention after 1986 where the foundations of their developments came from, is no justification for the "historians of exergoeconomics" to distort the truth by claiming that the present formalization of the theory is due entirely to Valero and co-workers, or that my approach is embedded in Valero's formulation, when exactly the opposite is true.

   Furthermore, the authors did not recognize that the approaches used by Valero and co-workers mainly apply to existing systems, whereas the approaches used by my group focus on the design optimization of new systems. I cannot see, for example, how my iterative exergoeconomic optimization method could be embedded in Valero's formulation. The section on thermoeconomics is full of misrepresentations and omissions of significant contributions by some authors (e.g., the group of researchers from the University of Padova [13-16]).
8. On page 10 in [1] the authors write "…[different authors] demonstrated that the optimal design point of a heat exchanger can be calculated only (the underlining is mine) by taking into proper account entropic losses, i.e., exergy destruction." Such an approach, however, has severe flaws and no optimal design can be obtained by it for the following three reasons:
   (a) An optimal design point can, in general, be obtained by considering the economic and the environmental performance together with the thermodynamic one, but not just the thermodynamic performance of a component.
   (b) A thermodynamic optimum obtained by this method is also questionable because the exergy destruction caused by friction is covered by mechanical (or electric) energy, whereas the exergy destruction caused by heat transfer is usually covered by the exergy of fossil fuels (or renewable energy). These exergy forms have not only different costs per unit of exergy but also different thermodynamic values, if we refer them to the same form of primary energy.

(c) The optimal design point of a heat exchanger cannot be obtained in isolation, because this depends on the relative position of the heat exchanger within the overall energy conversion system being studied.

9. An incorrect valuation of the pertinent factors occurs also in the applications of the exergy concept to societal systems (page 22) and in the approach of extended exergy accounting (pages 22 and 23) as well as in most environmental applications (pages 16 and 17) cited in [1]. A presentation of the principles that are violated by the above applications would exceed the framework of this Letter to the Editor. I will say only that the exergy concept is a very valuable thermodynamic concept. Therefore, it should not be mistreated by experts and discredited in the eyes of non-experts through questionable applications of this concept under the pretence of a false scientific advancement.
10. A plethora of publications is cited in each section of [1]. A large number of them is completely insignificant and some of them contain errors, whereas other important publications are left unmentioned. As an example of the latter I will give (a) the Ph.D. Thesis of Linnhoff [17], in which he pointed out some limitations of the exergy concept, when applied to heat exchanger networks, a finding that later led to the development of the "pinch method", and (b) several of my publications on power plants (e.g. [6,10,11,18-21], none of which is cited in section 5.1 "Power cycles and components" although the first author had received my complete list of publications.
11. Apparently the authors do not see any of the few but serious limitations associated with the exergy concept [22] as it has been developed until 2005. On the other side, they do not demonstrate clearly a very important strength of the exergy concept, that is the enhancement of the imagination, intuition and creativity of engineers that, for example, can lead them to develop completely new concepts of energy conversion processes based on pure exergetic evaluations (see example in [22]) or to significantly change and improve the design of a system under investigation (see the many important changes conducted in a complex IGCC power plant after finding out the magnitude of the exergy destruction in a mixing process of steam with gaseous products from the gasifier [19,23]).

I am very surprised by the form and the amount of bias exhibited by the authors in Reference [1]. A review article, which promises to be "critical" and "careful", "to clarify dubious points", and to respect "our scientific routes (the sources)" (all quotations are from the abstract of [1]), should show more respect to the target audience and should deliver what it promises.

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Authors' Reply to G. Tsatsaronis' Comments

We thank Professor Tsatsaronis for his frank comments and open criticism, because we feel that such an approach goes in the direction of a better scientific discussion on a very important issue like exergy analysis. In the following, we use the same numbering of his comments, and the numbers of the references are those of our extended bibliographic list (published on the IJoT website):

1) The comment is correct. In the course of the review/editing process of our paper, a short paragraph that was positioned before equation 1 was accidentally deleted (our fault!). We used the definition of the exergy "balance" for an open system (eqtn. 3.10.a in [168], the book co-authored by the Reviewer), and then proceeded to comment on the exergy of material streams.
2) The comment is partially correct. It is true that it is only the exergy of a stream that may take negative values while the exergy of a system is positive definite. But, it is not correct to "split the physical exergy into a thermal and a mechanical part" as suggested in the comment. For instance, for a gas stream and for a given T_0, there are regions in the *s/h* plane where the exergy is negative depending on particular combinations of both p and T [98, 2527,2528].
3) the Reviewer selected an *ad hoc* example to counter our general remark. The chemical exergy of pure C is about 34100 kJ/kg, and is the one for which the ratio ex/HHV is the highest (about 1.05 [2251]). For all types of coal, this ratio varies between 1.03 and 1.05. As for the Reveiewr's remark about liquid fuels are concerned, their chemical exergy is so close to their lower heating value LHV (3 to 6%) that in 99% of the relevant references we had access to, the difference is not even mentioned. See also [112,117,252,1814,1828,2145, 2279]
4) We clearly presented the exergy efficiency expressions 5), 6) and 7) as "*the definitions...that emerged from the debate of the 60'es*": the context clearly implies that this is a result that must be regarded within that timeframe! Nowhere in the paper a statement can be found that may give the impression that these are "*the only ones available*", as the comment goes. As for the claim made by the Reviewer about his own contributions ([5,6] in his comment, [2370,2409,2410] in our reference list), we must remark that the scope of our review paper was not that of discussing the numerous definitions of "exergetic efficiency" available in the literature (that would be a proper topic for a separate review). But, on the specific issue, it is our opinion that the "fuel-product" concept was already implicit (and perhaps explicit) in the "used exergy input-useful exergy output" definition provided by Baehr in 1968 [104]. It is true that Tsatsaronis and Valero developed this concept into the structured form of Thermo-Economics used today, but this is also acknowledged in our paper.
5) We surely cannot compete with the Reviewer in a semantic discussion about the Greek language, but the accepted comparative meaning of the "*en-*" and "*ex-*" prefixes in energy and exergy are "*internally capable of doing work*" and "*capable of having work extracted from*" respectively. The last meaning is explicitly indicated by Rant [1818] in his proposal to adopt "*exergy*" in lieu of "*availability*" (in German, *Arbeitsfähigkeit*, "capacity do to work").
6) It is well known that the Reviewer is a strong supporter of the word "Exergo-economics". The fact is though that the adjective "*exergiewirtschaftlich*" was in use already in the 60'es and 70'es to denote applications in which exergy calculations were used instead of energy calculations to assess the global performance of conversion processes. There have been public discussions in the past (in the presence of the Reviewer) in which it was agreed that the exergy costing principle is included in the method that goes under the name of Thermo-Economics. This said, every Author is entitled to adopt for his method the term he deems appropriate: but in a review paper, we felt we had to feature the concept more than the name.
7) The Reviewer raises here a point ("historical perspective") that is difficult to explain to newcomers to the field. To address the specific points mentioned in the comment, it suffices to recall that: a) Valero and coworkers did indeed produce the first complete formalization of the exergy costing method in their extensively quoted series of papers [2480,2481,2491]; b) They acknowledged the Reviewer' previous contribution on the basis of which they developed their method; c) Much earlier, between 1969 and 1970, Szargut had developed his own "cumulative exergy consumption" method [2222,2223] that he used to compute the cost of a product in "used exergy" units; d) Szargut did not like (and still does not like!) to include monetary considerations in his exergy analysis because his emphasis is on primary resource consumption. As a matter of fact, he published in 1978 an essay on the "consumption of natural resources" that for him is "the cost" (in an extended sense) of any production process [2233]; e) Valero has repeatedly stated that his method is not meant to be an "optimization" method. "Optimization" is a mathematical procedure that can be performed on the basis of any objective

function, be it exergy-based or not: in this sense, it is correct to state that “Thermo-Economics” and “Thermo-Economic Optimization” are two distinct animals; f) In our reference list, contrary to the statement by the Reviewer, we have included 30 papers by the “Padova school” (Lazzaretto & coworkers), so it it is not correct to say that we have “omitted” their contributions.

8) With regard to our point on the optimization of heat exchanging devices, the Reviewer makes some distinctions that we have not made, and misinforms readers about our presentation of the issue. What is clearly stated in our paper is that the “thermodynamically optimal” design can only be assessed by exergy considerations. Exergy destruction can be easily split into its separate components (thermal & mechanical destruction in this case), and this is actually the topic of an impressive series of papers in the past and current heat transfer literature ("Entropy Generation Minimization" which we also quoted in our paper). From this perspective, point c) of the Reviewer' comment is also misplaced, because - except for tutorial purposes- no heat exchanger is ever analyzed in isolation: the rejected heat can of course be re-used in the process, and this is indeed the basis for the Heat Exchanger Network (HEN) analysis. If one wants to perform a Thermo-Economic optimization, it is of course necessary to include as boundary conditions (= previously calculated or user's provided data) the exergy costs of each relevant input (so that the portions of these inputs that are destroyed by irreversibilities can be “costed” in turn), but we were not discussing this issue in the paragraph quoted by the Reviewer.

9) The point raised here by the Reviewer is unclear: we will try to “interpret” his critique and respond to this interpretation. If he means to criticize the (mis)use of exergy concepts made by environmentalists in their assessment of biological systems, we fully agree with him, and must remark that nowhere in our review do we show sympathy for “theories” that use exergy as a direct measure of environmental impact or for Authors who employ exergy to assess the “maturity” of a forest canopy. In fact, in the Conclusions we express some very critical remarks on such issues (points 5 and 6, pages 24 and 25). And our respective positions on these issues have also been explicit expressed in other papers. If, on the other hand, he means to express a critique to the Extended Exergy Accounting technique proposed by one of us (ES), we do not see the point in discussing the issue here: if there are “violations of fundamental principles” in EEA, it is possible to explicitly state these “violations” by making direct reference to the many papers published on the topic.

10) The publications listed in each Section of our article are indicative of the historical development of the concept, and quoting them does obviously not imply that we agree with either the methods or the conclusions stated therein. The complete bibliography provides though all the information that can be included in such a list (there are flags that identify the main topic for each reference, and it is there that interested readers should refer for further study). Incidentally, the Linnhoff Ph.D. Thesis is included therein [1390], in spite of the fact that, as it is well known, one of us (ES) has published a method of optimal HEN synthesis based on Sama's guidelines that counters some of the claims made by Linnhoff in his “Pinch” method. With reference to the papers authored or co-authored by the Reviewer, he sent us a list of 71 articles: our bibliography cites 85 of his works. Therefore, we do not think it can be said that we have shortchanged the Reviewer's contributions.

11) Every reader is entitled to having his own opinion of the “intentions” of the Authors, but we frankly do not see how one can say that we do not show appreciation for the “enhancement of the imagination, intuition and creativity” of engineers and physicists who make use of the exergy concept. Actually, we repeatedly state in the body of the paper and especially in the conclusions that there are still many fields (fluiddynamics and environmental analysis for example) in which it is likely that a more comprehensive use of exergy methods could lead to significant advancements.

We are of course available to further discussing these and other issues with the readers of IJoT, and are continuously updating our reference list: we shall be grateful to Authors who will communicate additions or signal omissions and misquotes, so that we can improve it and place an amended list on the Journal site.

Enrico Sciubba Gøran Wall