Int. J. of Thermodynamics
Vol. 10 (No. 1), pp. 1-26, March 2007

ISSN 1301-9724

A brief Commented History of Exergy From the Beginnings to 2004

Enrico Sciubba*
Dept. of Mechanical & Aeronautical Engineering
University of Roma 1 “La Sapienza”
Roma, Italy
enrico.sciubba@uniroma1.it

Göran Wall
Independent Researcher
Exergy-SE,
Mölndal, Sweden
gw@exergy.se

Abstract

This paper presents a brief critical and analytical account of the development of the concept of exergy and of its applications. It is based on a careful and extended (in time) consultation of a very large body of published references taken from archival journals, textbooks and other monographic works, conference proceedings, technical reports and lecture series. We have tried to identify the common thread that runs through all of the references, to put different issues into perspective, to clarify dubious points, to suggest logical and scientific connections and priorities. It was impossible to eliminate our respective biases that still affect the “style” of the present paper: luckily, some of our individual biases “cancelled out” at the time of writing, and some were corrected by our Reviewers (to whom we owe sincere thanks for the numerous and very relevant corrections and suggestions).

The article is organized chronologically and epistemologically: it turns out that the two criteria allow for a quite clear systematization of the subject matter, because the development of the exergy concept was rather “linear”.

This work is addressed to our Colleagues who are involved in theoretical research, industrial development, and societal applications of exergy concepts: if they extract from this article the idea of an extraordinary epistemological uniformity in the development of the concept of exergy, our goal will be achieved. The other addressees of this paper are Graduate Students taking their first steps in this field: in their case, we hope that consultation of our paper will prompt them to adopt and maintain throughout their career a scholarly valid method of research, which implies studying and respecting our scientific roots (the sources) but venturing freely and creatively into unknown territory.

In the Conclusions we try to forecast future developments: this is the only part of the paper that is an intentional expression of our own views: the previous historical-scientific exposition is instead based on verifiable facts and accepted opinions.

Keywords: Exergy, maximum work, thermo-economics, cumulative exergy cost, history of exergy.

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*Author to whom correspondence should be

1. Introduction

1.1 Why this paper

This paper originates from a very simple reflection: in the year 1970, about 50 articles on exergy (then called "Available Energy" in the US and "*Arbeitsfähigkeit*" or "*Exergie*" in Germany) were published in archival journals or presented at workshops and conferences; in 2004, this number by far exceeded 500. All major current Energy Engineering Journals publish on the average 1 or 2 articles on exergy-related concepts in each issue: since 2000 there is an International Journal of Exergy, which enjoys even in front of stronger competitors a satisfactory number of subscribers and authors. More and more graduate students use exergy analysis in their works, and classical exergy methods evolve very creatively. Every serious Thermodynamics textbook devotes at least one entire chapter to this topic, and Thermo-Economics (so strongly linked to exergy to be sometimes called "Exergo-Economics") is a topic for monographs of its own. Finally, and most importantly from an engineering viewpoint, industrial and institutional policymakers have started adopting exergy as the basis for their energy planning.

It occurred to us that there was no comprehensive historical account of the development of this very important concept and of its applications: most modern Thermodynamics books contain brief sketches of the line of thought that led to the introduction of the concept of "available energy" or "maximum potential work", but these notes are indeed too brief to provide the interested scholar with a complete impression of the very instructive sequence of individual steps that led from the recognition that "*the generation of motive power requires not a consumption of caloric, but rather its transportation from a hot to a cold body*" (Carnot, 1824) to the statement "*living systems thrive on exergy*" (Wall, 1997). A recent paper by Rezac & Metgalchi (2004), after giving a detailed analysis of the emergence of the term "exergy", concentrates on some present controversial issues in the attempt of resolving them, and thus does not provide a discussion of the extremely important and interesting series of debates that led from the "seminal years" (basically, and rather schematically, those before 1960) to the remarkable maturity of the exergy concept (roughly speaking, the beginning of the 1990s').

In this "brief commented history" our primary goal is to provide readers with a clear idea of the importance of the individual contributions to the path that led from the theory of caloric to the present day exergy applications in the fields of energy conversion, process optimization, diagnostics and management, analysis of Very Large Complex Systems (VLCS), information technology and sustainability analysis. We try to do this by two means: a very accurate bibliographic research that does not neglect any of the major contributions to the field; and a critical review of each source, in a consistent attempt to put things in the correct perspective, to describe this development as the evolutionistic combination of several "threads" that join into a well organized systematic theory for a while, then branch in different directions, sometimes converging again at a later stage.

1.2 Contents and limitations of this paper

This work is based on the references listed in the Extended Bibliography, which includes archival works and proceedings of major Conferences published before December 31, 2004[1]. In all instances in which a paper was published first in the Proceedings of a Conference, and then -under the same title- in a Journal, we quote here the Journal reference. Though every effort has been made to include original quotations, in some of the "classical" references (e.g., Carnot, Gibbs, Maxwell) we had to base our work on revised editions or/and translations. Also, all works originally published in languages other than English, French, German, Italian and Swedish were accessible to us only through English translations. Whenever possible, obscure or controversial points of all

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[1] With only two exceptions: a book by Szargut, published in 2005, the proofs of which were available to us in 2004, and a paper by Sciubba & Ulgiati, submitted in 2004 and published in 2005.

publications that appeared between 1950 and 2004 have been discussed with the authors: obviously, the responsibility of having gathered the correct interpretation rests entirely with us. The Bibliography may appear slightly biased towards publications in the fields of Mechanical Engineering, Energy Conversion Systems, and Resource Management: it is indeed so, because our familiarity with other fields where Exergy analysis is also applied (like Chemistry, Applied Physics, and Biochemistry for instance) is -unfortunately- rather limited. The enormous extent of the list of exergy references makes it unsuitable for direct inclusion in a paper like this: therefore, we have adopted a different, though less user-friendly, approach: the complete reference list is contained in a .pdf file available online under www.icatweb.org/vol10/10.1/Sciubba-Wall.pdf.

1.3 The modern definition of exergy

Exergy is defined as *the maximum theoretical useful work obtained if a system S is brought into thermodynamic equilibrium with the environment by means of processes in which the S interacts only with this environment.*

This is a rephrasing of a concept that was clear from the very beginning: already Gibbs' "availability function" (see Section 2) had the peculiar property of representing the "freely available work". Since there are many forms in which energy flows present themselves in nature, there are several corresponding forms of exergy. The most commonly used are listed in Table I.

The physical significance of the belov "equivalence table" is clear:

- The kinetic energy of a system traveling at a speed *V* with respect to a Galilean frame of reference can be -in principle- entirely recovered into <u>any</u> other form: potential (the ideal pendulum); heat (friction brake); mechanical (impulse turbine); electrical (piezoelectric effect).
- The same applies to gravitational potential energy and to all energy forms related to motion in a conservative force field.
- Mechanical work and electrical energy can also be freely converted into each other.
- Chemical energy cannot be entirely transformed into -say- mechanical work: the maximum "work" that we can extract from a system composed of a single pure substance depends not only on the chemical enthalpy of formation of that substance, but also on the difference between its concentration in the system and in the reference environment.
- Heat is the "least available" form of energy flow: the portion that can be converted into work depends on both the system (T_q) and reference (T_0) temperatures.

TABLE I. SPECIFIC EXERGY CONTENTS OF DIFFERENT ENERGY FLOWS

Type of energy flow	Specific energy	Specific exergy	Source	Notes
Kinetic	$0.5V^2$	$0.5V^2$	/	J/kg; follows from definition
Potential	$g\Delta z$	$g\Delta z$	/	J/kg; follows from definition
Heat	q	$q\left(1-\dfrac{T_0}{T_q}\right)$	/	J/kg; follows from definition
Mechanical	w	w	/	J/kg; follows from definition
Electrical[2]	$It\Delta V$	$It\Delta V$	/	J; follows from definition
Chemical, pure substance	Δg_G	$\mu-\mu_0+RT_0\ln\left(\dfrac{c}{c_0}\right)$	Wall 1977	$\mu-\mu_0=\Delta g_G=g_G-g_{G,0}$
Radiation[2]	I	$\sigma\left(T^4-\dfrac{4T^3T_0}{3}+\dfrac{T_0^4}{3}\right)$	Petela 1964	W/m^2; for black body radiation

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[2] Notice that for electrical energy and for radiation the notion of "exergy per unit mass" makes little sense. The correct extension of the definition is clear though in the context of every single application

Therefore, neglecting for the moment electrical energy[3], for an open system ***S*** identified by the thermodynamic parameters T_1, p_1, μ_1, V_1, z_1 that can interact only with a reference environment ***B*** at T_0, p_0, V_0, z_0, and in which the concentration of substance 1 is c_0, the specific exergy content, in J/kg, is a state function given by:

$$e_1 = h_1 - h_0 + \frac{V_1^2 - V_0^2}{2} + g(z_1 - z_0) + \Delta g_{1,0} + RT_0 \ln\left(\frac{c_1}{c_{1,0}}\right) - T_0(s_1 - s_0) \quad (1)$$

There are several important consequences of the above definition:

a) If the system ***S*** is in state "0" (i.e., all of its relevant parameters take the same value as those of the reference environment ***B***), its exergy is equal to zero: exergy is a thermodynamic potential, a general measure of "difference", and requires two different states for its definition.

b) There may be particular combinations of the values of the thermodynamic parameters such that $e_1 < 0$: the physical significance is that in this case, to bring the system in equilibrium with the reference environment, work must be done on the system by the environment;

c) If ***S*** proceeds from state 1 to state 2, its exergy variation in this process is also a function of state:

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

d) If in the transformation 1→2 some heat Q flows under whatever small but finite temperature differences) into S, the exergy of the state 2 is *smaller* than that of state 1 augmented of the quantity of energy Q: exergy has been *destroyed* in the process (namely, in the transfer of heat from higher to lower temperatures);

e) Any irreversibility in the process is reflected in a further decrease of exergy between the initial and the final state: denoting by $\Delta s_{irr,1\to 2}$ the irreversible entropy generation, we have:

$$\Delta e_{1\to 2} = T_0 \Delta s_{irr,1\to 2} \quad (3)$$

f) The reference state ***B*** (T_0, p_0, V_0, z_0, c_0) is necessary to the definition of exergy: for an isolated homogeneous system that cannot exchange either mass or energy with any other system, exergy is not defined;

g) If we consider processes that take place in finite times (always maintaining the assumption that they can be represented by a proper succession of quasi-equilibrium states), equations 1, 2 and 3 maintain their significance, if all the terms therein are substituted by their time derivatives;

h) If a system evolves in the presence of a varying environment (long geological timescales, or time- or site dependent external conditions), its exergy level varies accordingly, even if its state does not: this means, quite simply, that the maximum work we can extract from the system varies as well.

1.4 A word about notation

Different Authors have adopted wildly different notations: we shall uniformly refer to the notation provided in the Symbols list above. Where a different significance has been used, we shall identify it case by case.

2. The Early Beginnings: Carnot & Gibbs Work

It is widely recognized today that the exergy concept has its roots in the early work of what would later become "Classical Thermodynamics". If an "exact starting date" must be found, this can only be 1824, when Carnot (1824) stated that *"the work that can be extracted of a heat engine is proportional to the temperature difference between the hot and the cold reservoir"*.[4] It is correct to say that this simple statement led, 30 years later and after much labouring by Clapeyron (1832,1834), Rankine (1851) and Thomson (1852) to the position of the

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[3] For the sake of simplicity, and in line with current use, we do not include in Eqn. 1) other contributions, that may become important in specific applications: nuclear, magnetic, molecular vibration exergy, etc.

[4] It is still a matter of debate whether Carnot's "caloric" ought to be interpreted as "heat flux" or "entropy". The context he uses the word in is often (and clearly unintentionally) ambiguous.

second law of thermodynamics by Clausius (1850,1867). However, Gibbs (1873) who had earlier defined the thermodynamic function "available energy", was the first to explicitly introduce the notion of available work, including the diffusion term. He stated: "*We will first observe that an expression of the form*

$$-\varepsilon + T\eta - Pv + M_1 m_1 + M_2 m_2 \ldots + M_n m_n \qquad (4)^5$$

denotes the work obtainable by the formation (by a reversible process) of a body of which $\varepsilon, \eta, v, m_1, m_2, \ldots m_n$ *are the energy, entropy, volume, and the quantities of the components, within a medium having the pressure P, the temperature T, and the potentials* $M_1, M_2, \ldots M_n$. *(The medium is taken to be so large that its properties are not sensibly altered in any part by the formation of the body.)*"

Equation 4 (n.54 in Gibbs' work), is in exact correspondence with the present definition of exergy, equation 1 above.

Tait (1868), and Lord Kelvin as well, had also defined in his lectures something similar to Gibbs availability, but offered no extended discussion of the concept. Also Duhem (1904) in France and Caratheodory (1909) in Germany elaborated on Gibbs' "availability".

With no direct reference to Gibbs' work, the Frenchman L.G. Gouy (1889) and the Slovak A. Stodola (1898)[6] independently derived an expression for "useful energy" (in French *énergie utilisable*) as the diffeence between the enthalpy and the product of a reference temperature (which they specifically stated to be the ambient, or environment in modern terms, temperature) and the change in entropy, $T_0\Delta S$[7].

Maxwell (1871) and Lorenz (1894) presented some applications to the evaluation of thermal processes on the basis of entropy, and though neither of them explicitly mentions an availability function, it appears that they make a "mental use" of the concept.

Some reflections on Gouy's work appeared in France due to Jouget, who in a series of works (1906, 1907, 1909), applied the "dissipated work" concept (*exergy destruction* in modern terms) to thermal machines. Similar considerations, that imply a critique of the "first law" efficiency for thermal-to-mechanical conversion processes, were developed in the US by Goodenough (1911) and de Baufre (1925), in Germany by Born (1921) and in France by Darrieus (1930, 1931) and Lerberghe & Glansdorff (1932).

In the same years, J. H. Keenan in a series of fundamental works expanded and clarified the concept of exergy (in his notation, "availability"). His publication "A steam-chart for second-law analysis" (Keenan 1932) included explicit references to most of the earlier work. His textbook on thermodynamics (Keenan 1941) has exerted an important influence on his contemporaries, and substantially contributed to a more widespread knowledge about second law analysis in general and about the availability concept in particular.

Contemporary to Keenan, Fran Bošnjakovic (1935, 1938), a Croatian who taught in Dresden, Zagreb, Braunschweig and Stuttgart, laid the foundation of the German school of applied and theoretical Thermodynamicists, that were to further develop the concept of exergy two decades later. He published fundamental contributions to the identification of irreversibilities by a proper Second Law analysis, and stressed the importance of Gibbs' availability, that he called Work Potential (*Arbeitsfähigkeit*). In the same years, additional fundamental contributions were published by Rosin & Fehling (1929), who calculated the exergy of fuels, Emden (1938), and Rant (1947) who provided one of the first exergy analyses of a chemical process (soda production). Some interesting applications of the "available energy" concept to the analysis of heat exchangers were published in Russia (Gochstein 1939, Kirpitschev 1949) and in Germany (Glaser 1949).

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[5] Gibbs' original notation has been maintained here

[6] Aurel Stodola lived and worked in Switzerland, where he was a professor in the ETH- Zürich

[7] It is interesting that a paper by Gouy (1889b) was criticized by Duhem (1889), who claimed priority in the "discovery" of available energy (*energìe utilizable*). Gouy rebutted (1889c), but the issue was not conceded by Duhem. In modern terms, Duhem was referring to the Gibbs free energy function (u-Ts), and Gouy to exergy ($u-T_0s$): thus, Gouy was right!

In the US, Obert & Birnie (1949), published a seminal paper dealing with the assessment of the losses in a fossil fuelled power plant: the novelty was the use of availability to locate the most critical processes, a theme that will be tackled again about two decades later.

The legacy of those early years is too often forgotten: to a modern reader, it is apparent that in all the works quoted above, the concept of what we now call exergy analysis was entirely clear to all Authors (except perhaps for the very early ones: Carnot, Clapeyron and Clausius). The problem of the reference state had already been posed, but was not investigated at all in its implications; the possible effects of a Second Law analysis on the then scarcely available cost-efficiency correlations was also well understood; but the emphasis was generally placed on the possibility of decreasing the internal process irreversibilities and improve the "real efficiency" of the processes under examination.

3. The Definition of the Concept and of Its Fields of Application: 1950-1970

At a scientific meeting in 1953, the Slovenian Zoran Rant suggested that the term exergy (in German *Exergie*) should be used to denote "technical working capacity" (Bošnjakovic's *technische Arbeitsfähigkeit*). This was the proposal of a cultivated man: energy literally means "internal work" (from the Greek *en* [εν] and *ergon* [εργον]), and the prefix *ex* [εξ] implies instead an "external" quantity. Rant even published (1956) a linguistic essay to discuss international equivalent names for this quantity (he proposed *exergie* in French, *exergia* in Spanish, *essergia* in Italian and *eksergija* in Slavic languages). By adopting this name, all previous expressions, such as available energy, availability, available work, potential work, useful energy, potential entropy, etc. and later introduced terms such as essergy could in principle be abandoned. In practice, it took 50 years for Rant's denomination to become accepted worldwide: even at present, some US Authors still use the obsolete "availability" terminology.

As stated above, the modern definition of exergy is a rephrasing of Gibbs' original statement: *The exergy of a thermodynamic system S in a certain state S_A is the maximum theoretical useful work obtained if S is brought into thermodynamic equilibrium with the environment by means of ideal processes in which the system interacts only with this environment.*

Baehr gave in 1962 another definition, which is still widely used especially in energy conversion applications: *Exergy is the portion of energy that is entirely convertible into all other forms of energy.* (in German, *die Exergie ist der unbeschränkt, d.h. in jede andere Energieform umwandelbare Teil der Energie*). This definition is though misleading, because it implies that the "total energy" of a system is composed of two additive parts, one "convertible" (exergy) and one non-convertible (anergy)[8]. But there are several examples of systems with a negative anergy (solids below T_0, gases in certain ranges of $T<T_0$ and $p<p_0$, etc.), and this makes the use of Baehr's definition cumbersome.

The mature definition provided above had its roots in fifteen years of intense debate about the exergy concept: this debate took place mostly in Germany, with only marginal contributions from France, Switzerland, Italy and Sweden. It turns out, that in the same years (1950-1965) some prominent scientists from Russia and Eastern Europe (Martinowsky 1950, Gochstein 1951, 1962, 1963, Martinowsky & Alexejev 1955, Brodyanski & Meerzon 1960, Brodyanski & Ishkin 1962, Brodyanski 1963, 1964, 1965, 1967, Andreev & Kostenko 1965, Chernyshevsky 1967) also published fundamental contributions to the field: but their works were not directly available to the larger scientific body of the world, and therefore the two developments remained somewhat independent for years (the only link being

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[8] Baehr (1965) also discussed the function *anergy*, which we shall not consider here, since it is redundant (anergy=energy–exergy in his definition): but several Authors published on anergy to a large extent until recently (Erdelyi 1952, Almqvist 1964, Szargut 1966, Geisler 1969, Kalitzin 1969, Kurt 1969, Tuma 1971, Wachter 1977, Muschik 1978, Alefeld 1988a).

provided by Eastern European scholars who had direct access to the Russian sources).

At first, there was an effort to reformulate the thermodynamic problem-solving procedures in terms of entropy or exergy: thus, Gourdet & Proust (1950), Glaser (1953), and Rosin & Fehling (1929), among others, published enthalpy/exergy or enthalpy/lost work diagrams and developed process analysis procedures on these bases. Then, a major problem that was the matter of heated debates was the proper definition of the "efficiency" of a thermal process: in the works of Darrieus (1931), Hauser (1950), Hegelmann (1950), Grassmann (1950)[9], Frieder (1952), Lange (1953), Schmidt (1953), Grassmann & Kammerer (1954), Kammerer (1954), Nesselmann (1955), Bock (1956) and Mattarolo (1956) a critical review of "first law" efficiency definitions leads, on the basis of theoretical justifications, to a proposed "new definition" of a Second Law based performance parameter. It is noteworthy that this debate continued in the 1960s', and led to the modern efficiency definitions we are using today (see the books by Kotas 1985, Moran 1986, Bejan, Tsatsaronis & Moran 1996, Szargut 2005). In general, the goal of these Authors is to show that the thermodynamic performance of any process in which energy is converted from one form into another cannot be measured properly by First Law considerations, and that the energy in- and outflows ought therefore to be expressed in exergy terms.

In the same years, other Authors were involved in a theoretical debate about the foundation, the formulation and the applicability of exergy: the list includes among others Keenan (1951), Nesselmann (1952, 1953), Heller (1954), Marchal (1956), Denbigh (1956), Elsner & Fratzscher (1957, 1959), Evans (1958), Fratzscher (1959), Ackeret (1959), Bruges (1959), who all published original contributions to the field, and developed applications mostly in the field of energy conversion, heat exchangers and chemical processes.

Robert B. Evans (1961) showed that exergy (which he called "essergy") in itself incorporates other thermodynamic concepts such as Gibbs free energy, Helmholtz free energy, enthalpy, as well as the "availability" introduced by Keenan. In Evans' mind, even Gibbs free energy, Helmholtz free energy and enthalpy could easily -albeit with due attention- be replaced by exergy. The theoretical value of the concept of exergy (in his notation, still "availability") was addressed by Myron Tribus in his 1961 MIT course on Thermodynamics: his goal was to unify "classical" thermodynamics originating from the work of Carnot with statistical mechanics and information theory that had evolved from the atomic model to the new concept of quanta, and to reconcile the definitions of entropy. But Tribus' major accomplishment today is considered to be the "invention" of Thermo-Economics[10], see below, Section 7.

Theoretical developments, mostly aimed at a systematic analysis of the efficiency concept, were coupled with practical and often very innovative applications to the exergetic assessment of both existing cycles and processes in the works of Almqvist (1964) in Sweden, of Andreev & Kostenko (1965) and Brodyanski (1964, 1968) in Russia, of Fratzscher (1961), Gašperšič (1961), Rant (1961), Gasparovic (1962), Baehr (1962, 1963, 1965, 1968), Bošnjakovic (1963, 1965), Giesen (1965), and Heller (1968) in Germany, of Borel (1965) and Berchtold (1970) in Switzerland, of Chambadal (1965a) in France, of Medici (1966) and Codegone (1967) in Italy, of Gaggioli (1961) and Evans (1969) in the US, of Szargut (1954, 1956, 1957) and Petela (1963) in Poland. These works led not only to a more thorough understanding of the intrinsic loss mechanisms of engineering processes, but at times to quantum advances in cycle configurations, obtained by the more accurate analysis of the irreversibilities allowed by the exergy approach. Bošnjakovic (1961) edited a Special Issue of

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[9] In recognition of Grassmann's fundamental contributions to the field, the exergy flow diagrams of a process are called today "Grassmann diagrams"

[10] In spite of lack of formal acknowledgement on the part of Tribus, it is clear in hindsight that he ought at least to share this credit with El-Sayed and Evans, who were working in his group at the time. Both made fundamental contributions to the field (Evans in the years 1960-1980; El-Sayed is still active at the time of this writing). By contrast, Tribus did not publish any further on this topic.

the BWK, and Baehr (1965) edited another monography for the German Engineering Society (Verein Deutsche Ingenieure, VDI): both works contain several interesting and seminal papers on exergy analysis.

A mature topic requires a standard notation system: Szargut (1962, 1964) and later Weingaertner (1969) suggested two (different!) notational systems. As we shall see, this problem with notation was at least formally solved only much later (Kotas et al. 1987), but these early attempts were symptomatic: not only a single thermodynamic function (exergy) was referred to under different names (available energy, exergy, maximum potential work, work capacity), but there were almost as many definitions of "exergy efficiency" as there were Authors in the field. The dispute about the correct name to attribute to the function "h-$T_o s$" went on for years, but the definitions of efficiency that emerged from the debate of the 1960s' converged to three fundamental ones:

a) the "Second Law" or "exergy" efficiency

$$\varepsilon = \frac{useful \quad exergy \quad output}{used \quad exergy \quad input} \tag{5}$$

b) the degree of reversibility

$$\psi = \frac{exergy \quad of \quad "products"}{\sum(exergy \quad inputs)} \tag{6}$$

c) the coefficient of exergetic destruction

$$\xi = \frac{annihilated \quad exergy}{total \quad exergy \quad input} = \frac{T_O \Delta s_{irr}}{\sum(exergy \quad inputs)} \tag{7}$$

This debate about the correct efficiency definition was very relevant in the European literature (Grassmann 1950a,b, Kammerer 1954, Nesselman 1953, 1955, Bock 1956, 1957, Fratzscher 1961, Gasparovic 1962, Nitsch 1964, Borel 1965, Baehr 1968), much less in the US, where the definitions proposed by Keenan (1941), Obert (1948,1960) and Obert & Gaggioli (1963) were later refined and completed by Gaggioli (1961a, 1968), and almost uniformly accepted in the English literature. The development in Russia was parallel to that in Germany, due to the free exchange of information within the then Eastern Block.

At the end of the 1960s', thus, the theory of exergy was more or less completed, but only a small number of practical applications had been discussed (mostly to chemical systems and to energy conversion plants): in retrospect, we can say that in general the intellectual fallout of the exergy theory to industrial applications was slight if not absent at all.

4. The Mature Exergy Theory: After 1970

In our view, the extraordinary development and expansion of the exergy theory in the 1970s' and the exponential growth of its applications were due to two very different but equally influential causes: one is the concise, clear and stimulating discussion offered by some textbooks of the 1960s' (Baehr, Schmidt, Obert, Hatsoupoulos & Keenan), that prompted generations of graduate students in Engineering Thermodynamics to enter the field; and the other is the so-called "oil crisis" of 1973, that forced Governmental Agencies and industries in industrial Countries to concentrate on "energy savings". Increasing the "efficiency" of the chain of transformations that lead from raw resources to commercial products requires a thorough understanding of the location and of the relative importance of irreversible losses, and this is where, of course, exergy analysis comes to use.

In fact, most of the theoretical publications produced from the beginning of the 1970s' to the end of the 1990s' (with the exception of Thermoeconomics, see Section 7 below) deal with optimization procedures: the goal becomes that of defining the most convenient objective function that maximizes the exergetic yield of a process for a given resource input. Thus, the problem of correctly identifying the proper performance indicator for each elementary transformation or for an entire process is discussed in an extremely large number of publications worldwide. In this period, the first international workgroups are organized to facilitate the exchange of information by forcing different schools of thought to confront each other, and this results at once in an extraordinary broadening and deepening of the field.

There is no univocal way to summarize the enormous amount of work done in these years in the field of exergy: we chose here to separately consider theoretical developments (4.1); theoretical applications to energy conservation (4.2) and efficiency improvements (4.3); theoretical progress in chemical processes (4.4); the development of design tools (4.5); the study of material properties and of standard reference states (4.6); and more tutorial divulgatory works (4.7). Applications proper (i.e., procedures applied to practical cases) are examined in Section 5 below. It must be recognized, though, that a substantial degree of overlapping exists in most of the references quoted here.

4.1 Theoretical developments

The fundamental analysis and development of the exergy concept proceeded at a constant pace in these last 35 years. More and more scholars became involved in Exergy Analysis, and there is no Country which can be regarded as “leading the field”: though the vast majority of the works listed here were authored by US or German researchers, numerous fundamental contributions came from Russia and in general from the then Eastern Block, from Japan and from western Europe.

One of the most debated topics is of course the definition of all the implications of the exergy function and of its theoretical applications: Reistad (1970), Ussar (1970), Vlnas (1970), Weingaertner (1970), Wissmann (1970), Thoernqvist (1971), Bojadzev (1972), Keller (1972, 1982), Szargut (1972), Zubarev (1973), Chernyshevskyi (1974), Fratzscher (1974), Haywood (1974, 1979), Kalz (1974, 1975, 1976), Medici (1974), Naylor (1974), Andryuschenko (1975), Mayer (1975), Sawada (1975), Tribus (1975), Yasnikov (1975), Roegener (1976), Vivarelli et al. (1976), Yasnikov & Belousov (1976, 1977a,b), Berchtold (1977), Soerensen (1977a,b), Wachter (1977), Brzustowsky & Golem (1978), Kestin (1978, 1979), Klenke (1978, 1991a,b), Muschik (1978), van Lier (1978), Voigt (1978), Andresen & Rubin (1979), Borel (1979c), Kameyana & Yoshida (1979, 1980), Martinowsky (1979), de Nevers & Seader (1979a,b), Sussmann (1979a,b, 1980), Wepfer (1979), Woollert (1979), Yamauchi (1979, 1981), Andrews (1980), Ahern (1980b), Gaggioli (1980, 1983), Penner (1980), Silver (1981), Zschernig & Dittmann (1981), Enchelmayer (1982), Sato (1982, 1983, 1985, 1986a,b,c), Wall (1986), Gyftopoulos & Beretta (1987), Alefeld (1988b,c), Wang & Zhu (1988), Zilberberg (1988), von Spakowsky & Evans (1989a, 1990a,b), O’Toole & McGovern (1990), Lucca (1991), Dunbar et al. (1992), and Moran & Sciubba (1994), in their works made fundamental advances in the understanding of the thermodynamic meaning of exergy, contributed to a clearer definition of its derivation from prime principles, explained its theoretical advantages in the analysis of energy transformations, analyzed its correlation with irreversible losses and with the construction of a measure of an “energy quality scale”. Hatsopoulos & Gyftopoulos (1976a,b,c,d) provided, within a larger theoretical framework, a rational derivation of the "available energy" that is in essence equivalent to Baehr's maximum work concept, but avoids the introduction of an "anergy" function and extends Baehr's maximum work concept, i.e. the “exergy”, to any system (large or small; macroscopic or microscopic, including one-particle systems) and to any state (stable or not stable equilibrium).

Ageev & Martynov (1970), Opreschnik (1970), Baehr (1971), Brodyansky (1971), Alexiev (1973), Martinowsky & Meltser (1973), Martinowsky & Brodyanskyi (1974), Meltser et al. (1975), Ahern (1980a), Szargut & Maczek (1983) studied the implications of the exergy analysis on cooling and (Reinke 1971b, Adebiyi & Russell 1986) air conditioning processes.

Press (1976), Marshall & Adams (1978), Parrot (1978), Karlsson (1982), Haught (1984), Kutomi & Nobusawa (1984), Scholten (1984), Kar (1985), Altfeld et al. (1988), Suzuki (1988a,c), Badescu (1992), Svirezhev & Steinborn (2001), Wright et al. (2002) studied the exergy of solar radiation and/or its implications in the theory of solar collectors.

Glansdorff et al. (1955, 1956), Bauer (1970), Maltry (1971), Clarke & Horlock (1975), Lewis (1976), Li & Qiu (1992), applied the exergy concept to the analysis of aeronautic propulsive systems: this area is still under development today, with enormous implications for advanced flying vehicles, see Section 5.1 below.

Heat transfer is another field that did benefit from the introduction of exergy analysis: Harrison & Dean (1978), Evans & von Spakovsky (1980), Bejan (1982c), Boyd et al. (1982), Tapia & Moran (1986), Aceves-Saborio et al. (1989), Bejan & Sciubba (1992), Carrington & Sun (1992), Mereu et al. (1993), demonstrated that the optimal design point of a heat exchanger can be calculated only by taking into proper account entropic losses, i.e., exergy destruction. In a closely related field, Heat Exchangers Networks design and synthesis, exergy methods were developed by Fratzscher (1973, 1982), Berg (1979), Umeda et al. (1979), Vukovic & Nikulshin (1980), Pehler & Liu (1981), Ishida (1983), Vinograd et al. (1983), Chato & Damianides (1986), Gaggioli et al. (1991), Hale (1991), Maiorano & Sciubba (2000): all of these studies showed that the original Hohmann (1971) analysis could be extended to explicitly include exergy (entropy) considerations, resulting in faster procedures for optimal networks designs.

Heat- and work integration is also a field in which an exergy analysis leads to better thermodynamic optima: Beyer (1970), Gruhn et al. (1972), King et al. (1972), Berg (1974c), Khlebanin & Ten'kaev (1974), Yoon (1974) Rokstroh & Hartmann (1975), Sweeney et al. (1975), Edgerton (1979), Nishio et al. (1979), Umeda et al. (1979), Liu (1980, 1982a,b, 1983), Sophos et al. (1980a), Takamatsu & Naka (1982), Sciubba et al. (1984a,b, 1985a,b), von Spakovsky & Evans (1984), Nikulshin (1985), El-Sayed & Gaggioli (1988), Evans & von Spakovsky (1988, 1990), von Spakovsky & Geskin (1989), Tomlinson et al. (1990), Safonov et al. (1991), Streich et al. (1991) demonstrated that from a theoretical point of view exergy leads to better process integration, and therefore to more efficient resource use.

Buergel (1974) proposed to found the diagnosis of an industrial process on its exergy analysis: his work had no application until much later, see also Sections 5.6 and 8.3 for some recent applications.

Chimeck & Chandrasekhar (1984a,b) devised a model of Large Energy Systems and proposed to analyze them by means of exergy methods; earlier, Chlebanin & Nikolaev (1977) had produced a model of a supply-consumer system. Both works, which have some similarity with Szargut's method of Cumulative Exergy Content (see Section 8), went unnoticed for years, until the most recent developments published by Le Goff (1977), Wall (1983,1987,1988) Ayres (1998,2003), Azzarone & Sciubba (1995), Sciubba (1995), that led to a general method of Large Complex System Analysis.

Dehlin (1979) proposed to study the energy crisis of the 70'es by means of an exergy analysis: this seminal idea, also neglected at that time, resulted in later work in closely related fields by several authors (Wall 1981,1987a,b, Sciubba 1995, Ayres 2003,).

4.2 Energy conservation

A closely related field to process integration is of course energy conservation: actually, it is difficult to separate the contributions in these two fields. With this caveat, mention must here be made of the most important works in this topic, where Ross & Socolow (1974), Grassmann (1975), Hall (1975), Zlatopolskji & Zavadskji (1975), Gyftopoulos & Widmer (1977), Sussmann (1977), O'Callahan & Probert (1977), Graichen et al. (1978), Hanna & Frederick (1978), Michaelides (1979), van Gool (1979, 1980, 1992), Didion et al. (1980), Leidenfrost et al. (1980), Timmerhaus & Flynn (1980), Gaggioli & Wepfer (1981), Grant & Anozie (1981), Novusawa (1981), Soerensen (1981), Paolino & Burghardt (1982), Shinskey (1982), Kenney (1983, 1984), Rotstein (1983, 1988), Reay (ed., 1984), Alavarado & Iribarne (1990), gave a major impetus to the idea that energy "savings" in all processes can be attained only by judicious use of an exergy analysis.

Gaggioli (1977), Roberts (1982) and Stepanov (1984) introduced -though in a preliminary and still rather sketchy form- the related concept of *exergy audit* as a necessary substitute for the current energy audits. The concept was a fruitful one, was developed into an application by Valero et al. (1986), and gave origin to a series of publications in this area (Boyle & Lang 1990, Frangopoulos 1992, Özdogan & Arikol 1995, Nokicenovic et al. 1996, Cornelissen 1997, Belli & Sciubba 2001, Cornelissen & Hirs 2002, Dewulf & Langehove 2002a,b, Dincer 2002). Notice that all "national budget analysis methods" discussed in Section 9.5.3 below are also a direct application of this method.

Peters et al. (1977), Roth & Miley (1979), Petit & Gaggioli (1980), Rothstein & Stephanopoulos (1980) and Primus et al. (1984) proposed that exergy analysis be used in determining the future needs for research in the field of energy systems: this idea was also fruitful, and actually their works sparkled a series of proposals of new cycles and processes that stemmed from a basic exergy analysis of the drawbacks and of the limitations of "standard" processes.

4.3 Efficiency improvements

Another closely related field is that of process and component efficiency improvement: Munser & Dittmann (1971), Reistad & Ileri (1973), Zlatopolskji (1973), Bandura (1974), Bidard (1974), Hamel & Brown (1976), Slabikov (1976), Hevert (1979), Kaloferov (1979), Hussein et al. (1980), Kotas (1980), Khalifa (1981), Mansoori & Gomez (1981), Gerz (1982), Szafran (1982), Knoche et al. (1984), Horlock & Haywood (1985), Baines & Carrington (1986), Alefeld (1987), Tobias (1991), presented proposals for the improvement of process- and component efficiencies founded on an underlying exergy analysis. The definitions of the "second Law efficiency" they use are based on the studies conducted in the 1950s' and 1960s' mentioned above (Section 3).

4.4 Theoretical progress in chemical processes

Though the general trend that emerges from an analysis of the chemical engineering literature is that of directly applying the exergy concepts to process analysis, some noteworthy theoretical developments also took place: Streich (1975), Nishimoto (1976), Abrams (1978), Krishna (1978), Sakuma (1978), Hohmann & Sander (1980), Platonov & Zhvanetskji (1980), Henley & Seader (1981), Fonyo (1982), Andrecovich & Westerberg (1983), Al-Ahmad & Darwish (1991) studied separation, rectification, distillation and desalination processes, and Reinke (1971a), Standart & Lockett (1971), Szargut (1973), Ahrendt (1974, 1977), Riekert (1974, 1976a,b,c, 1979, 1980, 1981), Moran (1975), Semeniuk (1976), Vakil (1980), Teja & Roach (1981) Moore & Wepfer (1983), Richter & Knoche (1983), Rabinovitsch et al. (1984) and Siemons (1986) published contributions to several topics in chemical engineering, from reacting flows to combustion.

In the related field of Material Science, Shieh & Fan (1981, 1982) published a list of calculated exergies of materials with a complex physical structure.

4.5 Development of design tools

As industrial researchers became more accustomed to exergy analysis, a trend began to emerge towards the search for "standard" analysis and design procedures. Process analyses were published by Rademacher (1974), Rochelle & Andejewski (1974), Semenov et al. (1975), Urdaneta & Schmidt (1977), Hedman et al. (1979), Stepanov (1984), Hua (1986), until Kotas (1986) published the first systematic set of "exergy analysis procedures".

Thermodynamic diagrams were produced to be used as design aid tools by Tuma (1961), Glaser (1972), Reistad (1972), Baloh (1974), Daly & Harris (1979), Ishida & Oaki (1981), Oaki et al. (1981), Tapia & Moran (1981), Ishida & Ohno (1983), Zhu et al. (1988), Yantowsky & Lukina (1990), and. Ishida & Taprap (1992)

These developments were paralleled by extensive work directed to the determination of material properties, see Section 4.6 below.

In more recent years, the original "design procedures" developed into computer codes. It is impossible to provide a complete list of the computational procedures published in the last ten/fifteen years in the field of Applied Thermodynamics and Chemical Engineering, and we report here only the ones that can be considered "fundamental" on a time priority basis, with the obvious remark that successive numerical applications have remarkably improved on the quality of the few pioneering ones: Gaggioli et al. (1964), Gruhn et al. (1976), Johnson (1980), Krumm et al. (1984), Abtahi et al. (1986), Rosen & Scott (1986), Tapia & Moran (1986), Tsatsaronis et al. (1986), Valero et al. (1987), Melli & Sciubba (1987), Alconchel et al. (1989), Bidini & Stecco (1991), Wimmert et al. (1991), Ngaw (1998), Maiorano et al. (2002).

4.6 Material properties and standard reference states

As the application of exergy analysis to different processes and cycles developed, the need arose for a standard data base of material properties. The problem is that the calculation of the exergy of a material system on the basis of Eqns. (1) and (2) does not make much sense: it depends not only on the composition of the particular material, but also on the "reference state" that one takes for its components. Since it is obviously not possible to measure the concentration of each chemical constituent in the environment, the solution (first proposed by Szargut in 1957 but published in German in 1965 and in English only in 1980) is that of selecting a set of "reference substances" and determining their average concentration in the Earth's crust. These reference substances are the basis for the calculation of the exergy of the individual chemicals. The problem becomes of course that of defining a "standard reference environment". This is still an open issue today, and we shall examine the historical developments that led to the present situation. The basic problem is to define a congruent list of "fundamental chemical compounds" and their average concentration in a model of the Biosphere (the Earth's crust, the lower atmosphere, the hydrosphere). For instance, once the "fundamental state" of the water in the reference environment (which has by convention zero exergy) is taken to be that of the sea at $T_{ref} = 298$ and at a conventional salinity of 45‰, pure water at $T_{ref} = 298$ will have a *positive* exergy, equal to the negative of the desalination chemical potential. This is only an example: the problem of course does not lie with the reference state of water or air, but with that of some of the most common ores present in the earth crust, mainly silicates, carbonates, nitrates and oxides. Already in the 1960s', the problem was tackled by Bošnjakovic (1963), Fratzscher & Gruhn (1965), and Szargut & Styrylska (1965). In the following years, the problem of how to identify a convenient "average composition" of the lito-, hydro-, and lower atmosphere, was debated among others by Brodyanskyi et al. (1971), Kostenko et al. (1975), Ahrendts (1979, 1980), Ahern (1980), Gaggioli & Wepfer (1980), Sussmann (1981), Sorin (1984), Kotas (1985), Sorin & Brodyanskyi (1985), Szargut & Morris (1985), Morris & Szargut (1986), Szargut (1987), Fratzscher & Michalek (1989), Diederichsen (1991), Ranz et al. (1998), van Gool (1998): these Authors gave solutions that differ little from one another (the list of reference substances is almost the same), but even small differences in the reference elements produce substantial differences in the exergy values for most practical metals, fuels and construction materials. Valero et al. (2003) proposed an original method, based (partially) on substitution, in which the exergy content of an element is computed as the amount of exergy that would be expended to "replace" it in the mine. At present, in practice all exergy calculations are based on the "reference environment" published by Szargut et al. (1988), with some corrections due to Valero et al. (2002), Valero & Botero (2003) and Rivero & Garfias (2004),: notice that also Gaggioli et al. (2002) and Gaggioli & Paulus (2002) explored the theoretical implications of the exergy concept by "revisiting" the original Gibbs' works, and their findings have had some influence on the debate about the proper reference state.

Several Authors published their calculations of the exergy of different working media: we provide here a list of their works, with the warning that the reference states are not the same for all calculations. Rosin & Fehling (1929- oils & coal), Bock (1958 -oil and coal), Buimovici (1958- liquid fuels), Rant (1960a,d -gaseous & liquid fuels), Baehr & Schmidt (1963- oil and gas), Pruschek (1970- nuclear), Zakharov (1970- organic fuels), Valent et al. (1977- gas), Baehr (1979, 1986 -coal and oil), Cheng et al. (1980-coal), Srivastan (1988- coal), Stepanov (1995 - liquid & gaseous fuels) and Rivero (2002 - oil). The most general result was that -except for nuclear fuels- the exergies are approximately equal (within 2-5%) to the respective lower heating value. Gasperšič (1961), Baehr & Schmidt (1964), Knoche (1967), Rant & Gasperšič (1972) and Abu-Arabi & Tamimi (1995) computed the exergy of combustion gases.

Harmens (1975), Doering (1977a,b) and Ahern (1980) calculated the exergy of several refrigerants; Kabo et al. (1998) that of alkanes; Liley (2002) and Marquet (1993) that of moist air; Magaeva & Radnai (1986) that of non-electrolytes; Marin & Turegano (1986) that of electrolytical solutions; Poersch & Neef (1971) that of vapour/gas mixtures; Rao & Srinasavan (1997) that of Nitrogen; Runge (1968) that of Neon; Wandrasz (1968) that of a series of Fe-C alloys.

Brodyansky & Kalinin (1966), Opreshnik (1970), Eckert & Fratzscher (1987), Rosen & Scott (1988), Fratzscher & Michalek (1989), Etele & Rosen (2000), Paulus & Gaggioli (2001), Serova & Brodyansky (2002) provided methods for accounting for a changing environment: this can be of importance in the case of process calculations in the presence of seasonal temperature or concentration variations, or of pressure, temperature and composition variations with altitude.

4.7 Tutorial divulgation works

Though less important from a scientific standpoint, an extensive literature exists of a more tutorial and divulgatory character. We are not referring to monographic books (which are listed separately in Section 9), but to articles in archival and non-archival journals that contributed to propagate the idea that exergy analysis was a "better" tool for engineering design and analysis purposes. Examples are the archival articles by Alexander (1977), Fratzscher & Beyer (1981) on the status and trends of exergy analysis, of Tsatsaronis & Valero (1989) on Thermo-economics, and the more divulgative ones by Wertan (1972), Townsend (1980), Vrugging & Collins (1982), Mc Cauley (1982, 1983), Soma (1982, 1983, 1985a,b) and Spreng (1991). There are also "state-of-the-art" papers (in less specialistic journals or in encyclopaedias) that have played a non-negligible role in bringing up the subject among academic and non-academic specialists, like those of Bruges (1955,1957), Tribus (1958), Keenan et al. (1974), Schipper (1976), Tsatsaronis & Cziesla (2002a,b), Serra & Torres (2003), Valero (2003), Valero & Torres (2003), Valero et al. (2003).

5. Engineering Applications: 1950-2003

Applications of exergy methods to the analysis of energy-conversion and chemical processes are very abundant in the archival literature: the list provided here is only indicative. The subdivision by topic is also somewhat arbitrary, and interested readers are encouraged to consult the original papers for better reference.

5.1 Power cycles and components

5.1.1 Steam power cycles: In this area, after the very fundamental works of the early years (Birnie & Obert 1949, Roegener 1961, Salisbury 1969), and after the later papers by Keller (1959), Danila & Leca (1966), Gaggioli et al. (1975), Sciubba & Su (1986), Lozano & Valero (1987), Alconchel et al (1989), Acar (1997), Rosen (2001), Espirito Santo (2003) no relevant studies have been published. The reason is obviously the exceptional maturity of this type of plants: it is likely that a renewed interest in these studies will be prompted by the recent emphasis on "zero CO_2" cycles for the production of hydrogen, see Fiaschi & Tapinassi (2002), Zhang & Lior (2003), Soufi et al. (2004). However, most processes proposed to date are of the cogenerating type (electricity + H_2, or gas/steam/CO_2 cycles) and fall under point 5.1.4 here below.

Daniel (1996) presented an interesting study of a reciprocating steam engine.

5.1.2 Gas turbine cycles: The gas turbine cycle is still a preferred topic for exergy analysis. Several papers continue to appear in archival publications, confirming the idea that the Brayton cycle (especially with the most recent advances in materials and blade cooling technology) will see some breakthrough in the near future. Chambadal

(1965a,b), Gasparovic & Stapersma (1973), Bandura (1974), Vivarelli et al. (1976a,b), Harvey & Richter (1994), Pak & Suzuki (1997), Fiaschi & Manfrida (1998a,b), Abdallah et al. (1999), Di Maria & Mastroianni (1999), Falcetta & Sciubba (1999), Lombardi (2001), Zheng et al. (2001), Alves & Nebra (2002), Jin et al. (2002), Song et al. (2002), Aronis & Leithner (2003), Ishida (2003), Kopac & Zemher (2004) (steam-injected GT), Sue & Chuang (2004) all dealt with both global and local aspects of the problem, and some of the works explicitly addressed transient operation regimes.

5.1.3 Renewable energy cycles: The most suitable candidate for an exergy analysis is of course solar technology (both for low and high temperatures). Works in this area were published by Bejan (1982), Edgerton (1981) (solar energy systems), Çomakli & Yüksel (1994), Luminosu & Fara (2004) (solar collectors). Photovoltaics (especially the new ones, which combine heat and power production) were also explored, for instance by Ahmad & Mohamad (2000).

5.1.4 Other Energy conversion cycles: The combined and the cogenerating cycle are the most frequently studied processes, as testified by the works of Andryushenko (1963), Avgousti et al. (1989), Bilgen (2000), van Poppel et al. (2003), Rosen et al. (2004), (cogeneration); Bejan (1984), Bram & De Ruyck (1995) (CO_2 combined cycle); Chlebanin & Nikolaev (1977), Brzustowski & Golem (1978), Didion et al. (1980), Bitterlich et al. (1982), Sciubba et al. (1984 a,b), Gaggioli ed. (1985), Yantowsky et al. (1992) Sawillion & Thöne (1994), Tuma (1995), Sahin et al. (1997), Torres & Gallo (1998), Cownden et al. (2001), (combined cycles and other energy systems); Reistad & Gaggioli (1970), Pak & Suzuki (1997) (total energy systems). Some trigeneration examples are studied in Sciubba & Guerrero (1985), Gao et al. (2002) (poly-generation), Marrero et al. (2002).

Fuel cells are also a system often subject to an exergy analysis: Dunbar et al. (1993), Bedringas et al. (1997), Douvartzides et al. (2004) (fuel cells combined cycle); Kazim (2004).

Buchet (1973), Dunbar et al. (1995), Lior (1997a,b) presented exergy analyses of nuclear cycles; Rakopoulos & Giakoumis (1997,2004) and Caton (2000) studied reciprocating internal combustion engines; Hepbasli & Akdemir (2004), Koroneos et al. (2004) and Yildirim & Gokcen (2004) analysed a geothermal energy conversion process; Kalina & Brodiansky (1997) analysed the so-called ammonia-based Kalina cycle.

Glansdorff et al. (1956) were the first to publish an exergy analysis of a jet engine. Only much later Bauer (1970), Clarke & Horlock (1975), Lewis (1976), Malinowsky (1984) produced complete system analyses. And it took another 20 years before Bejan & Sims (2001), Etele & Rosen (2003), and Rosen & Etele (2004) presented exergy analyses of flying vehicles, considered as “energy conversion systems”. Cszys & Murthy (1991), Brilliant (1995) and Bottini et al. (2003, 2004) developed specific applications to scramjets.

5.2 Heat exchangers and Heat Networking

Exergy is well suited to perform a systematic study of heat exchange processes, and the book by Bejan (1982) provides several examples of what he calls an “entropy generation rate” analysis aimed at the identification of optimal designs. This proved to be a very productive field: heat exchangers proper were analysed by Elsner (1960), Chambadal (1965a), Bejan (1977), Petela (1984), Aceves-Saborio et al. (1989), Hale (1991), Lampinen & Heikkinen (1995), Bejan et al. (1998), Bisio (1998), Cornelissen (1999), Sorin et al. (2000), Abbassi & Aliehyahei (2004) (evaporation plate).

District heating was analysed by Cornelissen et al. (1996), Cornelissen & Hirs (1997), , Skorek & Kruppa (2003) (low-T heating) and Ozgener et al. (2004).

An exergy-based method for the optimal synthesis of heat exchanger networks was originally proposed by Pehler (1983), but was later developed into a systematic method by Sama (1983), and further by Gaggioli et al. (1991), Sama (1995a,b), Maiorano & Sciubba (2000), Maiorano et al. (2002).

Other applications in the field were published by Beyer (1970, 1972, 1978) (sugar production), Ramayya & Ramesh (1998) (latent heat storage), Errera et al. (2000) (bulk cooling), d'Accadia et al. (2003) (vapour compression heat pump), Gomri & Boumaza (2003) (solar heat pump), Ionita (2003) (apartment heating), Mahmud & Fraser (2004) (porous stack),.

5.3 Cryogenics

Since the exergy content of a stream increases below the environmental temperature, cryogenics is yet another field in which an exergy analysis can provide new and original design insight. The first papers in this topic were published by Nesselmann (1938), Martinowsky (1950) (whose book inspired many later German textbooks on the subject), Grassmann (1952) and Bock (1956). In the 1960s', Fratzscher (1964), Grassmann (1964), Peculea (1964) and Szargut & Maczek (1964) published interesting contributions.

Among the more recent papers, we like to quote here those by Ahern (1980), Benelmir et al. (1991) and Wall (1991) (optimisation), Srinivasan et al. (1995), Adewusi & Zubair (1997), Cornelissen & Hirs (1997,1998), Fartaj et al. (1997), Ahmed et al. (1998), Lu et al. (1998), Torres et al. (1998), Liu & You (1999), Rosen (1999), Rosen et al. (1999,2000) (cold thermal storage), Chen et al. (2001), Aprea & Greco (2002) (R-22 substitution), Badescu (2002) (solar heat pump), Bilgen & Takahashi (2002), Szargut (2002), , Yumrutas et al. (2002), Rakhesh et al. (2003), Varani et al. (2003) (Li-Br absorption cycle), Kilicaslanb et al. (2004) (vapour compression cycle), Sahoo et al. (2004) (absorption cycle), Snoussi & Bellagi (2004) (heat driven cooling system), Somasundaram et al. (2004).

5.4 Chemical processes

The conversion of chemical exergy into thermal exergy, and vice versa the injection of thermal exergy to promote and maintain a chemical conversion is of great importance for industrial and power conversion applications. Already Rant (1947) in his doctoral dissertation discussed a Second Law analysis of a soda plant. An influential work was that of Denbigh (1956), in which the concept of "chemical reaction efficiency" was discussed. Bock (1959), Rant (1960), Fratzscher & Nitsch (1961) and Fratzscher & Schmidt (1961) expanded the exergy analysis to homogeneous and heterogeneous reactions. Gašperšič (1961) computed then the exergy of combustion gases, useful for gas turbine applications and for many industrial processes.

Fundamental papers were published by Zakharov (1970), Ahrendts (1974, 1977), Nydick et al. (1976), Eckert et al. (1987), Futterer et al. (1991), Guoxing & Zijung (1997). Combustion was also extensively studied: Knoche (1967), Rosen (1996), Szwast & Sieniutycz (1997), Anheden & Svedberg (1998), Sorin et al. (1998), Rasheva & Atanasova (2002), Woudstra & Stelt (2003).

In the most recent years, the emphasis is being shifted towards an exergetic or thermo-economic analysis of specific applications: Gaggioli & Petit (1977), Gaggioli & Rodriguez (1980, Gaggioli & Wepfer (1980) (coal gasification); Ishida (1983) (coal liquefaction); Ishida & Taprap (1992) (multi-component distillation); Kirova-Yordanova et al. (1994,1997,2003), Kirova-Yordanova (2002) (ammonia synthesis); de Oliveira & van Hombeeck (1997) (petroleum separation); Tober et al. (1999) (aniline process); Sorin et al. (2000) (multi-step processes); delle Site & Sciubba (2001) (ethanol production); Okazaki et al. (2002), Akiyama & Maruoka (2003) (methane conversion); Syahrul et al. (2002) and Poswiata & Swast (2003) (drying); Atanasova & Lasheva (2003) (precipitate production); Geuzebroek et al. (2004) (CO_2 removal),

5.5 Distillation and desalination

Since desalination processes convert thermal or mechanical exergy into chemical exergy (they increase the exergy content of salty water to make it "fresh" or potable), this is also a field of extensive investigation. The first paper in the field is that by Freshwater (1951), but the later monographs by Spiegler & Laird (1966) and El-Sayed (1970) have exerted an important influence on designers of desalination plants.

On the general topic of "desalination", we can quote here the papers by Abrams

(1978), Umeda et al. (1979), Henley & Sieder (1980), Andrecovich & Westerberg (1983), al-Ahmad & Darwish (1991), al-Sulaiman et al. (1995), Hamed et al. (1996), Sauar et al. (1997), El-Nashar et al. (1998), El-Nashar (1999), Garcia-Rodriguez & Gomez-Camacho (2001), Slesarenko (2001), Cerci (2002), Bona et al. (2003) and Darwish (2004).

The important issue of the optimal integration of desalination processes with topping thermo-mechanical ones was studied among others by Gaggioli et al. (1989) and Sommariva & al. (1997).

The contributions by El-Sayed, Evans and Tribus that led to the development of Thermo-Economics are discussed in Section 7 here below.

Kaiser & Gurlia (1985) introduced the concept of "ideal column" to apply exergy concepts to distillation processes; Cornelisson et al. (1995), Rivero (2001, 2002) and Husain et al. (2003) studied crude oil distillation, while Fitzmorris & Mah (1979), Naka et al. (1982), Fonyo & Rev (1981,1982), and Ishida & Ohno (1983) analysed chemical distillation processes.

5.6 Industrial & agricultural systems analysis

There are several application studies in the literature, most of them presented at Conferences and only few published in archival journals. The first paper (Elsner & Fratzscher, 1957) dealt with a boiler, a thermo-mechanical conversion plant, and a steam locomotive! Bosnjakovic (1959) was a good second with his exergy analysis of an industrial oven. Due to the very extensive range of studied applications, a complete list is difficult to compile, but the following one gives an idea of the breadth of the field: Akpinar & Sarsilmaz (2004) analyzed the solar drying of apricots; Aoki (1992), Fan et al. (1985) agricultural systems; Auerswald (1980), Baloh (1981) and Guallar & Valero (1988) a sugar factory; Çamdali et al. (2004) the cement production process; Akiyama et al. (1991), Çamdali & Tunc (2003), Chinneck (1983), Costa et al. (2001), Keenan et al. (1974), Masini et al. (2001), Michaelis et al. (1998), Morris et al. (1983), Szargut (1961), Ziebik & Stanek (1997) metallurgical processes; Barclay (1981) and Brodyansky & Ishkin (1962) the liquefaction of gases ; de Lieto et al. (1983) and Gaggioli & Wepfer (1981) building systems; De Lucia & Manfrida (1990) and Sun & Xie (1991) glass production; Dinale et al., (1992), Eskin & Kilic (1996), Ghamarian & Cambel (1982), Segovia et al. (2003) and Sieniutycz (1990) fluidised beds; Dincer (2002), Kato (1981) and Szwast (1990) the drying of solids; Gemici & Öztürk (1998), Gong & Karlsson (2004), Helik (1972) and Wall (1987) pulp paper processes; delle Site & Sciubba (2001), Midilli & Kucuk (2003), Sama (1989) biomass; Mozes et al. (1998), Öztürk (2004) solar cooker; Petela (1984) the grinding of solids, Saidi & Allaf (1999) the vortex tube, Taprap & Phutthame (2003) and Trägårdh (1981) the food industry; Abbakumov (1975) and Brauer & Jeschar (1963) industrial ovens.

6. Environmental Applications

Due to its very definition, it is intuitive that exergy can be regarded as some sort of thermodynamic indicator of the environmental impact of a process: unfortunately, the simple equivalence "exergy discharge into the environment = pollution" (Crane & al. 1990, 1992, Masini et al. 2001), though -albeit only in part- qualitatively correct, is incorrect from a quantitative point of view.

The first papers approaching this problem are those by Kraft (1974) and Szargut (1974), in which an attempt is made to assess the global impact of "energy systems" on the environment, with specific regard to the problem of the so-called "global warming". Mejer & Jørgensen (1979), Jørgensen & Mejer (1981) and Eriksson (1984) tried to explicitly apply the thermodynamic function "exergy" to the modelling of ecological systems: this line of research was later developed to full potential by Jørgensen (1992).

The problem has two facets, because the "ecological cost" of what we generally call "pollution"[11] can be computed in exergetic or in monetary terms: accordingly, some Authors (Eriksson et al., 1976, Wall 1977, 1978, Szargut 1978, 1986, Valero &

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[11] For an important reflection on the difference between what "pollution" represents for humans and for Nature, see (Wall 1997)

Arauzo 1991, Ayres et al. 1998, Makaritchev 1998, Zaleta et al. 1998, Zhang & Reistad 1998, Rosen & Dincer 1999) have computed the amount of exergetic "consumption" that "makes up" for the pollution, while others (Frangopoulos 1992, von Spakovsky & Frangopoulos 1994) have attempted to calculate the amount of monetary expenses for remediation. This second line of thinking leads directly to a Thermo-economic treatment, developed in fact by Valero (1998).

Resource recovery and recycling (to minimize discharge into the environment) is another closely related issue: papers on this topic have been published by Otoma & Goto (1979), De Lucia & Lanfranchi (1991), Ayres et al. (1998), Connelly & Koshland (2001), Dewulf & van Langehove (2002a), Lattouf & De Oliveira (2003), Sciubba (2003).

A life-cycle analysis for the correct treatment of the problem of the effluents has been proposed by Finnveden & Östlund (1997), Ayres et al. (1998), Cornelissen & Hirs (2002) and Dewulf & van Langehove (2002b).

The "environmental issue" is connected to the concept of "sustainability": the problem is particularly complicated, because sustainability is not a thermodynamic concept (Second Law denies "strong" sustainability!), and the issue is often marred by a commixture of technical and non-technical considerations. Papers on this topic have been published by Jørgensen (1992), Sciubba (1995a,b), Cornelissen (1997), Rosen & Dincer (2001), Wall & Gong (2001), and Dewulf & van Langehove (2002b): most present research in this area is aimed at finding an implicit or explicit functional use of exergy in the analysis of environmental issues.

Valero and coworkers (Valero & Botero 2002, Valero et al. 2002) coined the word "Exergo-ecology" to denote the analysis of environmental effects performed by means of exergy costing methods (see Section 7 below).

7. The Exergy Cost ("k") or Cumulative Exergy Content ("CEC")

Szargut (1978, 1987) must be credited as the originator of this method: actually, there is a long history of his previous little-known publications in Polish journals (starting already in the early 70'es) that build up to the final concept. Michalek & Stritzel (1990) applied the CEC method to some process industries, and Szargut et al. (2002) made further extensions. The central idea is that, since exergy is additive, any production chain may be seen as a series of elemental processes, each one of which adds some exergy to its inputs, destroys some exergy in its internal irreversibilities, and delivers a product endowed with some "added exergy value". The "final" product, i.e., the one that is generated at the end of the chain, has therefore a Cumulative Exergy Content (expressed in kJ/unit) that can be exactly computed once the production process is known. Recursive application of this technique leads to the calculation of one (or more, if the same product is generated by different production lines) exergy cost ("k"[12]) or cumulative exergy content ("CEC") for each commodity that we use in our society, including dematerialized ones like power, electricity etc. In Valero's formalization, the theory of the exergy cost asserts that it is possible to express the exergy of the products as a process-dependent function of the exergy of the inputs:

$$E_O = \Pi(E_i) \qquad (8)$$

Where the matrix Π is called the *transfer function* of the process, and depends on the process configuration, i.e., on the connectivity of the system. Π is easily obtained by properly assembling the exergy "balances" (including the exergy destructions) of the individual components (Valero et al. 1986, Sciubba 1995c). It must be remarked that the "Cumulative Exergy Consumption" and the "Exergy Cost" are, by definition, exactly the same: in spite of their rather different formalization, Szargut's and Valero's methods are indeed equivalent.

8. Thermo-Economics

The idea of linking Thermodynamics and costing considerations was explored first by Lotka (1921), Keenan (1932), Benedict

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[12] In Valero's original works, the exergy cost is denoted by a capital B. We had to change the symbol here, because "B" in this paper denotes the reference environment

(1949, published by Benedict & Gyftopoulos in 1980) and Gilbert (1956): the clear concept that emerged from their very general papers was that entropic considerations ought to be somehow accounted for in monetary cost calculations. Beckmann (1953), Henatsch (1957) and Szargut (1957) explicitly addressed the problem of the correct cost allocation between co-generated products (steam and power).

At the beginning of the 60'es that, almost simultaneously and by independent investigators, 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, Fratzscher 1965, Elsner 1965, Nitsch 1965, Bergmann & Schmidt 1967) and *Thermo-Economics* (in the US, Evans 1961, Tribus 1961, Tribus & Evans 1962, Evans & Tribus 1965, El-Sayed 1970). The basic idea of this method is to apply the usual procedures of Engineering Accounting, linking the prices of components to their operating parameters and to their exergetic efficiency, and pricing not the unit mass, but the specific exergy content of a stream (material or energy).

If we attribute a monetary cost to the exergetic inputs, this cost will be incrementally increased in the various steps of the process, due to the hardware and operating costs that "add to the value" of the successive production steps. Since in general the production chain is not strictly linear, some outputs from a certain component may be split and constitute the inputs for two or more of the remaining components; conversely, two or more outputs may constitute the input to a different component. Therefore, to compute the cost of the final outputs (the product streams) we need to properly allocate the hardware costs (capital & maintenance, for instance) among the various outputs of each component: this can be done mathematically (as shown by Valero et al. 1986) by augmenting the matrix Π with a proper set of auxiliary "cost allocation equations". The result is again a matricial function in the form

$$C_O = B(E_i, C_i) \qquad (9)$$

Since both E_i and C_i are in turn functions of thermodynamic parameters x_j, material properties π_k, hardware design variables d_i and allocation criteria a_m (where each suffix varies in its proper range), the cost function C_O can be rewritten formally as

$$C_O = \Phi(x_j, \pi_k, d_i, a_m) \qquad (10)$$

Notice that Thermo-Economics can be used in two different ways:

a) For a given configuration, one can use Eqn. 10 to find the specific cost $c_{O,n}$ (€/J) of the unit of exergy of each product. The extensive cost $C_{O,n}$ (€/kg, €/J, €/unit) is then found by multiplying $c_{O,n}$ by the proper flux of that product (kg/s, J/s, units/s). This is the original Tribus-Evans-El Sayed formulation, and constitutes a noticeable improvement with respect to the usual engineering accounting procedures, that do not take into account the exergy destructions in each component. The method is especially useful when more than one product is co-generated by the same production line;

b) If the configuration can be changed (by inserting additional components, eliminating others or simply varying the connectivity of the process), or if some of the process parameters or design variables can be changed, one can find the "optimal" design point by means of a constrained optimization procedure, in which the "fixed" arguments in Eqn. 10 act as constraints, and the parameters that can vary are the independent variables of the optimization. Lagrange multipliers were used by the first Authors (see for instance Kotas 1985, Evans 1988, Gaggioli et al. 1988): the multipliers λ turn out to be the marginal costs of the respective products. Later, more general, powerful and effective multi-variable optimization techniques have been applied (Fietzel et al. 1985, Frangopoulos 1992, Sorin et al. 1992, Uche et al. 2003).

The word Thermo-Economics (TE) was first used by Myron Tribus in his MIT lectures, and the original developments are due mainly to El-Sayed & Evans, and independently to Elsner & Fratzscher. A substantial contribution was provided by Gaggioli, Reistad and Wepfer in the US, who had to struggle at the time to find access to archival energy journals for TE-related topics.

A more modern approach, based on an elegant and very general matricial notation, was developed only much later, by (Valero et al. 1986 a,b,c; Valero et al. 1992 a,b,c), and goes under the name of Structural Thermo-Economics. It is based on the construction of an "exergetic cost matrix" assembled on the basis of the process connectivity and of the rules of exergy costing, and is formally entirely equivalent to Eqn. 9 above. The present formalization of the theory and applications of TE is due entirely to Valero and coworkers, 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.

Of importance is also the more industry-oriented approach proposed by Tsatsaronis et al. (2003), Cziesla & Tsatsaronis (2003), as well as the efforts by Szargut (1987) to include taxation effects into the pricing structure.

An extension to explicitly include into the accounting a modelled set of environmental externalities has been later proposed by Szargut (1987) and, independently, by Frangopoulos & von Spakowski (1993). Further extensions, to account for unsteady operating conditions and to include life-cycle effects have been proposed by Frangopoulos & von Spakovski (1993) and Tober et al. (1999) respectively.

The early papers on this topic constitute a difficult reading, because of the uncertainties associated with the determination of the exergy unit costs, the different and often contrasting terminology employed, and the not always crisply defined general framework of the analysis. Szargut (1957, 1969), Gruhn (1965), Panzer (1965), Bergmann & Schmidt (1967), Ponyatov (1968), El-Sayed (1970), El-Sayed & Evans (1969a,b), Fratzscher (1973), Kalinina & Brodyanskyi (1973, 1974), Borel (1974), Beyer (1978, 1979a,b), Grubbstroem (1980, 1985) are the most relevant papers in this field.

After the publication of Valero's works in 1986, the interest in TE increased steadily, and today most energy journals offer at least 2 or 3 papers on TE in each issue. A remarkable example of critical comparison of contrasting theories and concepts in thermoeconomics is provided by the so-called "CGAM" project (Valero et al. 1994) that gave origin to four papers by different Authors who tested their respective approaches on the analysis of a Combined Powerplant benchmark (Frangopoulos 1994, Tsatsaronis 1994, Valero et al. 1994, von Spakovsky 1994).

Subsequent applications are very diverse in scope, breadth and depth: Alvarez et al. (2003) (fuel cell GT cycle), Avgousti et al. (1989), Ben et al. (1989), Borgert & Velasquez (2003, 2004) (Kalina cycle), Frangopoulos & Nakos (2003), Kakaras et al. (2003) (fuel cells), Jassim & Khir (2004) (rotary air regenerator), Modesto et al. (2003) (industrial cogeneration), Nikulshin et al. (2003) (energy supply networks), Gallo & Gomes (2003) and Rivero et al. (2003) (combined cycles), Sahoo et al. (2004) (absorption systems), Torres et al. (1989), De Oliveira et al. (2003) (trigeneration systems), Rücker & Bazzo (2003), Silva et al. (2003) (cogeneration), Velasquez & Sandrini (2003) (steam from biomass).

9. The Extension of the Concept and the Inclusion of Externalities: 1980-2003

A concise modernization of the exergy theory, with a strong emphasis on possible applications to the analysis of complex systems was presented by Göran Wall (1977), who called exergy "a useful concept in resource management", to meet the increasing needs of a sustainable development (though the word "sustainable" had not yet been coined at that time).

In Wall's paradigm, the concepts of human and industrial ecology are the only tools capable of modeling the social metabolism, i.e. the use of natural resources as carriers of exergy in the society. Exergy (destruction) can be seen as the driving force of the evolution of all systems, from the smallest living cell to the largest cosmic object, and it is of the utmost importance that its supply, distribution and use, for all purposes, are performed in such a way that its destruction be minimized. Through the work of Wall, exergy applications have been extended to include problems such as "natural resource accounting" considering both energy and material resources, life cycle exergy analysis, environmental indicators and evaluation of an environmental taxation that encourages sustainable development.

Customarily, the production cost of a commodity is expressed by a "Production Function" *f* whose operands are the products of the unit costs of each production factor by an intensive measure of the factor itself (J for energy, kg for materials, € for capital and environmental cost, work-hours for Labour):

$$c_j = f(C, M, E, L, O) \qquad (11)$$

It has been shown (Fratzscher 1965 & 1967, Szargut 1978, Wall 1978c, Grubbström 1980 & 1985, Momdjan & Sciubba 1993) that it is possible to construct a physical costing paradigm in which the energy-, material and Environmental cost-related "Production Factors" are represented in terms of exergy.

It is clear that once the three factors E, M and O, which are *per se* incommensurable with each other, are made homogeneous by adopting exergy as the common quantifier for all streams that flow "in" and "out of" the process, the irreversibilities in the production chain are better accounted for: this is the basis of the Extended Exergy Accounting (Sciubba 2000, see below). There is no problem in expressing Energy- and Material inputs and outputs in terms of exergy: how to assign a proper exergy cost to Environmental effects is still the topic of some fundamental debate (Szargut 1973 & 1974, Frangopoulos & von Spakovsky 1993, von Spakovsky & Frangopoulos 1993, Valero 1995a & 1998, Sciubba 1999).

9.1 Process conversion efficiency

Aoki (1992) studied the behaviour of complex processes at steady state; Lior (2002) studied the implications of exergy analysis on some possible trends in the energy conversion systems; Michalek & Stritzel (1990) analysed some material-processing technologies; Sciubba & Ulgiati (2005), in a much broader context, provided an exergy analysis of a corn-to-ethanol distillation process. Tekin & Bayramoglu (2001) provided an analysis of the sugar production process; Wang et al. (2003), Chen et al. (2003a,b) studied the exergy destruction of a class of turbulent flows in a pipe.

TABLE II. CLASSICAL COST-FORMATION MODEL: FIVE PRODUCTION FACTORS

Capital Production Factor	C=	$f_K K$	f_K = unit cost of Capital K = Capital (in monetary units)
Material Production Factor	M=	$S(f_{Mi} m_i)$	f_{Mi} = unit cost of the *i-th* material m_i = mass flow rate of the *i-th* material (kg/s)
Energy Production Factor	E=	$S(f_{Ek} en_k)$	f_{Ek} = unit cost of the *k-th* energy flow en_k = energy content of the *k-th* stream (kJ/s)
Labour Production Factor	L=	$S(f_j W_j)$	f_j = unit cost of the *j-th* Labour input W_j = Labour (in workhours)
Environmental "Production Factor"	O[13]=	$S(f_p m_p)$	f_j = unit environmental cost of the *p-th* effluent m_p = mass flow rate of the *p-th* effluent (kg/s)

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[13] The symbol "O" here denotes the initial letter of the Greek word ’ὀικος (=home) whence all the "eco-" prefixes have stemmed

9.2 Process structure optimization

Aceves-Saborio et al. (1989) studied the design optimization of heat exchangers; Aglieri-Rinella et al. (1991) provided an exergy-based optimization of a steam generator for industrial applications; Bejan & Siems (2001) applied exergy destruction minimization to the identification of the quasi-optimal design of an aircraft, considered as an energy conversion system; Chinneck (1983) applied a sort of exergy-enhanced network theory to devise the optimal structure of some thermal processes;

Dekhtyarev (1978) and El-Sayed (2002) used an exergy analysis as a guide to preliminary design optimization of cyclic processes, while Doldersum (1998) applied the same approach to identify the optimal process modifications (revamping) of thermal processes. The important problem of optimal synthesis had been discussed previously already by El-Sayed & Gaggioli (1988), Evans et al. (1981), Gaggioli et al. (1991) and Sama (1995a,b): notice however that an exergy-based approach to the optimal design of a HEN had been previously proposed by Pehler (1983). Based on these two latter works, Maiorano & Sciubba (2000) and Maiorano et al. (2002) proposed an exergy-guided intelligent design assistant for Heat Exchanger Networks (HEN). In the same line, Monanteras & Frangopoulos (1999) devised an optimal design procedure for a fuel cell-based powerplant. Szargut (2002c) presented a slightly more general formulation for optimal design, which can be in principle applied to any process.

9.3 Exergy-based diagnostics

In two seminal works, Torres et al. (2002) and Valero et al. (2002) elaborated on an original proposal previously made by Buergel (1974), and developed a method to identify malfunctions in a component of a process by studying their impact on the exergy efficiency of other connected components. Further work in this area was published by Carraretto et al. (2003). A similar method has been also distilled into an Artificial Intelligence procedure by Biagetti & Sciubba (2002, 2004). Lazzaretto & Toffolo (2003), Verda (2003), Verda et al. (2003), Zaleta et al. (2003) developed a TE-based diagnostic method, in which the fault is identified by a "localised" increase in the thermo-economical cost-formation chain of the process: this line of work culminated in the so-called "TADEUS" project (a complete TE-Diagnostic procedure with an application), which was published in 2004 byValero et al. Though it is true that the actual effect of a malfunction can be correctly measured only by the corresponding increase in the exergy cost of the output, in our opinion an exergy-cost or a TE analysis of a malfunction follows a diagnostic act, and cannot anticipate it. It must be remarked though that both Valero and Verda express in their papers exactly the opposite opinion.

9.4 Exergy life-cycle assessment

This is a line of research that has had little momentum since it was proposed by Cornelissen & Hirs (1997), but appears to deserve more attention as present resource-management strategies move towards "sustainability". In fact, all the most recent methods of exergy analysis (including Thermo-Economics, Cumulative Exergy Consumption and Extended Exergy Accounting) take a life-time perspective, and -at least in theory- trace the "exergetic history" of a commodity from well or mine to final disposal. It is interesting to remark that the seed of Cornelissen's work may be found in earlier work by van Gool (1980, 1987) who started as an energy analyst and only later (van Gool 1990) became an exergy practitioner. Cornelissen & van der Berg (2003) extended this line of research introducing explicit sustainability considerations.

9.5 Complex system analysis, biological and societal systems

9.5.1 Complex Systems: The analysis of complex systems by exergetic methods consists in the adoption of exergy to express the energy content of each material or immaterial input- and output stream and of exergy efficiencies to quantify the system "performance". Relevant papers are those of Radebold (1974), Le Goff (1977), Morf (1978), Morf (1978), Otoma (1979), Soma (1983), Corliss (1986), Mansson (1986), Malaska & Groenfors (1991), Valero & Arauzo (1991), Rosen (1992), Schaeffer & Wirtshafter (1992), Özdogan & Arikol

(1995), Sciubba (1995), Connelly & Koshland (2001a,b), Nikulshin (2001), Gogus et al. (2002), .

9.5.2 Biological Systems: The largest number of publications in this area come from the "emergy" arena[14]. The initial idea can be traced back to the works of Joergensen & Mejer (1977, 1981), in which the Authors proposed to employ exergy as an indicator for biological processes (emergy had been devised for this purpose a decade earlier). Further refinements of this approach were discussed in Joergensen (1981) and Jizhong et al. (1996).

Joergensen (1992a, 1992b, 2001, 2004)[15], Joergensen et al. (1995, 2002a,b), Salomonsen & Jensen (1996), Bastianoni & Marchettini (1997), Marques et al. (1997), Xu (1997), Fonseca et al. (2000), Ray et al. (2001), Ray et al. (2001), Debeljak (2002), Demirel (2004), Fabiano et al. (2004), Fath & Cabezas (2004), developed several applications of an approximate exergy analysis of biological systems. Their works are, in our opinion, characterised by a high degree of originality and biological insight, but also by a lack of thermodynamic rigor: most of their applications rely on equilibrium principles and are applied to living beings, which by definition are systems far from equilibrium. The original works from which such lines of research stemmed are those of Knizia (1986) and of course the famous book by Schrödinger (1944), both of which were much more rigorous and did not make recourse to somewhat arbitrary "additional principles of thermodynamics".

Another line of research was directed to the definition of the modes and methods of exergy analysis of complex (networking) structures, always considered as systems interacting with the Biosphere: Nielsen (1995, 1997), Bendoricchio & Joergensen (1997), Bianciardi & Ulgiati (1998), Svirezhev (1997, 2000), Szargut (2003) published relevant works in this field.

9.5.3 Societal Systems: The first author to explicitly compute the exergy flow diagram of a Nation was Reistad (1975), who analysed the US system. The method was extended and improved about ten years later in a much-referenced series of works by Wall (1986, 1990, 2002) and Wall et al. (1994). Societal sectors have also been analysed from a 2-nd Law point of view, both in isolation: Le Goff (1977), Widmer & Gyftopoulos (1977), Nakicenovic et al. (1996), Ossebaard et al. (1997), Ptasinski & Koymans (2004), and as an integral part of a "societal control volume": Azzarone & Sciubba (1995), Ileri & Gürer (1998), Ertesvag & Mielnik (2000), Ertesvag (2001, 2004), Mei & Wall (2001), Wall & Mei (2001), Ayres et al. (2003).

The sustainability issue was discussed on the basis of an exergy approach by Cornelissen (1997), Kalf et al. (1997), Cornelissen & Hirs (1999), Cornelissen et al. (2000) and Cornelissen & Boersma (2001).

9.6 Extended exergy accounting

On the basis of a method developed by Sciubba (1998), which may be traced back to an idea published much earlier by Grubbstroem (1985), a new field of exergy analysis has emerged under the name of Extended Exergy Accounting ("EEA"). The method is a standard exergy analysis in which Szargut's CEC (see Section 7 above) is augmented by additional exergy flows that represent the exergetic equivalents of the

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[14] A discussion of the concept of emergy is beyond the scope of this paper. Interested readers may consult the original work by Odum (1970), or the brief and critical discussion presented in Sciubba & Ulgiati (2005).

[15] In 1948, C.E.Shannon, then at the Bell Laboratories, published a paper on information theory, *A mathematical theory of communication*. This was to be literally the start of a new science, *Information Theory*. In the context of this review paper, the importance of Shannon's work resides in his definition of an "entropy function" that is depending on the amount of information bits needed to completely define the "state" of a (not necessarily thermodynamic) system. The implication is obvious: an exergy value can be attributed to information, or putting it in other words, exergy is a measure of information content. Similar concepts (using a different definition of entropy) were developed by L.Brillouin (1953), and in 1957 E.T.Jaynes published a formal derivation of Gibbs' results using Shannon's entropy as a starting point. Though the matter is far from being clear in all of its implications, we prefer to adopt Kline's point of view here (Kline 1999): he found some fundamental faults in the extension of Shannon's entropy to classical Thermodynamics that invalidate the equation entropy=information (NOT the concept: just the dimensional equivalence). There are other ways to link exergy to information content, as we shall discuss in Section 11 below.

Capital, Labour and Environmental Remediation Production Factors (whence the name "extended"): the final "balance" is given by an equation formally identical with eqtn. 8 above. Both in its method and in its formalization, EEA is very similar to Valero's Structured Cost Theory (Section 8), though there are some non negligible differences in the form of the Transfer Function Matrix Π. Applications have been published by Milia & Sciubba (2000), Belli & Sciubba (2001), Sciubba (2001, 2002), Ertesvag (2003), Ptasinski & al. (2004).

10. Books

There are several books that treat exergy in a (more or less) monographic sense. The list provided here is probably the most complete and updated reference available today. Exergy researchers are advised to carefully consult these monographs, which offer different and often contrasting definitions and approaches, but definitely provide an enlightening view of the development of the exergy concept through the years.

The old works by Maxwell (1871), Tait (1868), Jouget (1909) and Goodenough (1911) are only of historical interest today. Interesting are the early developments presented by Bosnjakovic (1935) and Keenan (1941), this second one with fundamental applications that are still relevant after over 60 years. Also fundamental are the two books (in German) by Schmidt (1953) and Baehr (1962) that have influenced two or three generations of european researchers in the field. Other books on exergy are those of Martinowsky (1950), Gourdet & Proust (1950), Marchal (1956), Bruges (1959) and Ford et al. (1975).

More modern approaches are presented by Ahern (1980), Kotas (1985) (which is a recommended first lecture for graduate students in the field), Moran (1982) (very detailed and tutorial, also a recommended lecture), and Sussman (1980). The two works by Bejan (1982, 1988) are less monographic and contain a substantial portion of fundamentals, presented and discussed with a very original approach. The later monographic work by Bejan et al. (1996) is presently the most referenced book on Exergy analysis and Thermo-economics, and finally, the two books by Szargut (Szargut et al., 1988, and Szargut, 2005) constitute essential (albeit advanced) reading for both fundamental theory and applications.

11. Review Papers, Nomenclature Definitions and Bibliographies

The first review paper on exergy was published by Gasparovic (1961) and -almost concurrently- by Bosnjakovic ed. (1961): for obvious reasons, both included rather few publications. Later reviews worth mentioning are those compiled by Szargut (1964), which includes several useful and difficult to find references to works published by Authors in the then Eastern Block; by Baehr ed. (1965) and by Soma (1983), who presented a relatively small list of references and is rather limited in his selection criteria. Another useful source was the ACS Symposium Series 235 edited by Gaggioli (1983). The most comprehensive reference list (before the one attached to this paper) is that compiled by Wall (1987), which is very extensive even if not always precise. Other lists were published by Kotas et al. (1987); by Elsner (1993), which is more a historical overview of the theory and concepts than a real review paper; by Cornelissen (1994) in his Ph.D. dissertation; by Kay (1989, placed on the web in 1998); and by Rezac & Metgalchi (2004), who approached the subject from a more theoretical viewpoint, privileging concepts rather than completeness.

12. What Next? A (Biased) Look Into the Future

To foretell "whereto exergy analysis is going" is a double-edged argument: furthermore, the present authors are obviously rather strongly biased towards "Complex Systems" issues, and this might have influenced our conclusions here below. However, with the obvious *caveat* that such a prediction has to be taken with care, we can conclude that:

1) It is clear that Process Analysis will see more and more applications of Exergy methods. The present ever increasing number of publications in the field of organic- and inorganic Chemical Processes is a sure sign that accounting for real process

irreversibilities provides a better grasp of even complex processes such as distillation, petroleum cracking, etc.

In the Energy Conversion arena, there is today practically no process- or cycle analysis that does not include exergy considerations. This can be regarded as a very mature field, and it seems that the exergy methods are on their way to being regarded as standard industrial analysis procedures. There are still issues that need to be addressed in more depth and breadth, even at fundamental level: life-cycle exergy analysis of real processes, the influence of dynamic operation, the analysis of Very Large Complex Systems are examples. But we cannot detect theoretical hindrances on the way of constant advances and refinements of both theoretical and application-oriented exergy analysis.

Exergy-based optimization procedures exist, and more will undoubtedly be developed in the future. A present limit here is posed by the immense computational resources required by a complete optimization of systems with a high number of relevant parameters (each one of which constitutes a degree of freedom for the optimization).

2) It is also rather clear that Thermo-Economic methods will be more and more extensively adopted in the assessment of industrial processes and production cycles. There are still some issues as to the inclusion of environmental considerations into TE, and some major research effort is needed in this area, because the presently proposed solutions are not entirely satisfactory.

3) System synthesis is most likely the "next frontier": the possibility of formulating an optimization problem in which the independent variables are not only related to process parameters but also to process configuration is very real already at present: at least formally, the problem can be solved by MILP techniques (Muñoz & von Spakovsky 1999), Genetic Algorithms (Toffolo & Lazzaretto 2002), and Artificial Intelligence techniques (Melli et al. 1992, Sciubba & Melli 1998). Practical applications to simple systems (i.e., systems with few independent variables) have already been published. Large complex systems still require excessive computational resources for their "optimization". Notice that since the goal of system synthesis is the minimization of the "product cost" (monetary or exergetic), the costing functions can be conveniently expressed by the methods of Thermoeconomics, Cumulative Exergy Content and Extended Exergy Accounting. Thermoeconomics seems to be the one that is more likely to be used in practical applications in the near future, EEA being a good but rather distant second. Interesting are also some attempts based on heuristics (like the search for an optimal geometry of a gas turbine blade, or similar CFD-based exergy destruction calculations, see next point here below), that show potential of being transformed into automated -albeit extremely computationally intensive- procedures.

4) It is possible, and highly desirable, that the application of exergy methods be expanded into the realm of thermo-fluiddynamics applications. Under the continuum hypothesis, the local entropy generation rates can be computed by most present CFD codes, and therefore the exergy destruction in heat- and fluid flow can be properly assessed even at local level: this may lead to the concoction of more effective design methods for fins, compact heat exchangers, ailerons, surface treatment and/or injection/suction, etc. This is an area in which not much has been published to the date of this writing (see though Bejan 1982, Carrington & Sun 1992, Fewell et al. 1981, Harrison & Dean 1978, Kouremenos 1971, Natalini & Sciubba 1994 & 1999, Poulikakos & Bejan 1982, Sciubba 2004), but which might open up entirely new perspectives as energy (exergy!) efficiency becomes a more important issue.

5) The interconnection of the exergy concept with "environmental issues" (taken in their broader sense) is also likely to be explored in more depth. Exergy *per se* is NOT a measure of environmental impact, but in essence at the end of the life cycle of any device, plant and product, the exergy "balance" of the extraction-transformation-production-distribution-use-disposal cycle shows how many primary exergy resources have been actually used up (consumed), and there are already some studies that address

the issue of designing "more exergy-conscious" production cycles to attain a higher degree of sustainability.

6) In a closely related field, namely the analysis of "living" systems, we are not so optimistic. Exergy is a thermodynamic function defined for equilibrium or quasi-equilibrium processes, and its extension to far-from-equilibrium systems (as all living systems are) is not to be taken for granted. Thus, unless some breakthroughs in irreversible thermodynamic are made, we neither foresee nor favour exergy analyses of plants, forests, bacterial colonies and the like, and much less those of human beings.

In some living systems analyses, the use of an "information exergy" is proposed. This exergy is considered to correspond to the genetic "information" contained in the DNA. We must remark that a) there is no proven link between exergy and information except in a strictly physical sense specified under point 7 here below, and b) "thermodynamics of life" -if such an object exists!- goes well beyond the concept of "transmitting information".

7) Cumulative Exergy Consumption methods are likely to see more and more applications in the near future. They provide an extremely clear picture of the "resources" used up (incorporated in) the production of goods. They can be extended to include immaterial services, and (like in EEA) they can account for labour and capital as well, thus paving the way to the calculation of an "exergy cost" of commodities measured in kJ/unit (as in CEC and EEA) instead of €/kJ (as in Thermo-Economics). An open problem for CEC is its neglect of Labour and in general of all immaterial production factors; but this issue is being already debated in the literature, and it is likely that a satisfactory solution can be found. This would be good news, because there are numerous proposed applications to the analysis of societal systems that could greatly benefit from the existence of an accepted paradigm.

8) Application of exergy analysis to microscopical physics appears problematic. The current paradigm prescribes that, once either the continuum and/or the equilibrium hypothesis are abandoned, exergy becomes a matter of convention. In their 1976 work (see Section 4.1 above) Hatsopoulos and Gyftopoulos argue against this view, and propose an extension of the definition of exergy that applies also to microscopic non-equilibrium systems. In our opinion, the issue awaits clarification, and some additional research is definitely needed in this field.

9) The few attempts to define "the exergy content of one bit of information" (based on mind-experiments performed on boxes and "pistons" with 1, 2 or 3 atoms) strongly suffer from a lack of well-founded theoretical development. Notice that in their above quoted works, Hatsopoulos and Gyftopoulos (1976a,b,c,d) argue quite strongly from a theoretical and mathematical standpoint that such an informational framework contains a built-in violation of the 2nd Law. A more formal critique has been raised by Kline (1999, see footnote #15 on previous page). We must stress that in our view the only reasonable way to account for information is at present a CEC or an EEA approach, in which the amount of physical resources expended for the generation of 1 bit of information can actually be computed on the basis of an analysis of the process that generates this bit: also this view is, of course, in dispute.

10)On the opposite, an application of exergy analysis to macroscopic physics (astronomy, for instance) appears possible, even if no example is known to us as of 2004 except for Jørgensen et al. (1998). Since exergy includes both gravitational and radiation effects, it is in principle possible to perform an exergy "balance" of a galaxy (the "reference environment" being the 3K residual radiation field). Far fetched as it may seem, such an analysis might lead to interesting finding on the entropy generation rate of the Universe.

List of Symbols

B	Reference system, Biosphere
c	Molar concentration
c_p	Specific heat, J/(kg K)
e	Exergy, J/kg
g	Gravitational constant, m/s^2
g_G	Gibbs free enthalpy, J/kg
h	Enthalpy, J/kg
I	Electric current, A
IR	Radiative energy flux, W/m^2

q	Specific thermal energy, J/kg
R	Gas constant, J/(kg K)
s	Entropy, J/(kg K)
t	Time, s
T	Absolute temperature, K
u	Internal energy, J/kg
V	Velocity w.r.t. Galilean frame, m/s
w	Specific work, J/kg
z	Elevation, m

Greek symbols

ΔV	Electrical potential, Volts
ε	Exergy efficiency
η	Energy efficiency
μ	Chemical potential, J/kg
σ	Stephan-Boltzmann constant, $W/(m^2K^4)$
ψ	Degree of irreversibility
ξ	Coefficient of exergetic destruction

Suffixes

0	Reference conditions
irr	Irreversible

References

The present paper contains over 2600 references: it was clear from the onset that it would have been impossible to include a regular “Reference List”. We decided instead, with the permission of the IJoT Editor, to attach here a link to the Journal web-site where the cited works are properly listed. We will be grateful to readers who suggest additions or corrections to this list.

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