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Entropy and exergy in irreversible renewable energy systems

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A R T I C L E I N F O

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Exergy and entropy generation analysis of the open systems allows to obtain a measure of how far the open real systems deviate from equilibrium with their environment. A link between entropy generation maximum principle and the exergy analysis of engineering and natural systems is suggested in order to use the exergy and entropy approach to improve the renewable energy systems.

Contents

1. Introduction

Engineering and technical thermodynamics is the science which studies both energy and the best use of available energy resources: energy and energy transformations, including power production, refrigeration, and relationships among the properties of matter.

Energy is a thermodynamic property of systems that, during interactions, can change from one form to another, leaving its total amount constant [1].

The second law of thermodynamics states that energy has quality as well as quantity, and actual processes occur in the direction of decreasing quality of energy [1]. Thermodynamics plays a key role in the analysis of systems and devices in which energy transfer and energy transformation take place [1]. I. *Dincer and Y.A. Cengel emphasize that Nature allows the conversion of work completely into heat, but heat is taxed when converted into work and, also, a careful study of this topic* [energy] *is required to improve the design and performance of energy-transfer systems.* [1].

Entropy has been proven to be the quantity which allows us to describe the progress of non-equilibrium dissipative processes [2]. Irreversible open systems develop following the thermodynamic path which maximises their entropy generation under present constraints [3]. Moreover, from 1995 to 2012 the *principle of maximum entropy generation*, S_g, has been proven for the open systems [4–6].

This extremum principle for the variation of the entropy due to irreversibility, called entropy generation, represents an important result in thermodynamic engineering because it is a global theoretical principle for the analysis of the stability of open systems.

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The aim of this paper is to link the entropy generation maximum principle and the exergy analysis of engineering and natural systems. To do so in Section 2 the entropy generated will discussed in relation to the open irreversible systems, in Section 3 the required link between entropy generation and exergy will be pointed out and in Section 4 some applications will be discussed.

2. Entropy generation

Classical science emphasized equilibrium and stability, while, recently, it was pointed out the role of fluctuations, instability and evolutionary processes: irreversible processes are observed everywhere symmetry is broken. In thermodynamics the distinction between reversible and irreversible processes has been introduced by using the concept of entropy so that its formulation is fundamental in order to understand thermodynamic aspects of self-organization, evolution of order and life as we observe in Nature [1].

The introduction of entropy in classical thermodynamics is related to equilibrium state and reversible transformation. In that context, entropy is a state function depending only on the equilibrium state of the system considered and only entropy differences can be evaluated [3]. The introduction of entropy generation comes from the necessity to avoid inequalities and use only equation from mathematical point of view. Nothing is really *produced* or *generated* [3,7]. Indeed, the second law states:

$$\oint \frac{\delta Q}{T} \leq 0 \tag{1}$$

defining the total entropy as [4]:

$$S = \int \left(\frac{\delta Q}{T}\right)_{\text{rev}} = \Delta S_e + S_g \tag{2}$$

then S_g is the entropy generation, that is the entropy variation due to irreversibility, defined as [7]:

$$S_g = \int_{\tau_1}^{\tau_2} \dot{S}_g d\tau \tag{3}$$

with:

$$\dot{S}_g = \frac{dS}{d\tau} - \sum_{i=1}^{n} \frac{\dot{Q}_i}{T_i} - \sum_{\text{in}} G_{\text{in}} s_{\text{in}} - \sum_{\text{out}} G_{\text{out}} s_{\text{out}} \tag{4}$$

and τ_1 and τ_2 the initial and final time of the process, Q the heat exchanged, T the temperature of the thermostats, s the specific entropy and G the mass flow. It is always $S_g \geq 0$ The quantity ΔS_e should be better defined as the entropy variation that will be obtained exchanging reversibly the same fluxes throughout the system boundaries. Then entropy is not more than a parameter characterizing the thermodynamic state and the term due to internal irreversibility, S_g, measures how far the system is from the state that will be attained in a reversible way [3,7]. In the second law analysis the definition and identification of the thermodynamic system is fundamental. The open thermodynamic system has been analytically introduced in terms of advanced analysis in Refs. [3,7]. Here its phenomenological description is summarized as follows. Let us consider an open continuum or discrete N particles system. Every ith element of this system is located by a position vector $\mathbf{x}_i \in \mathbf{R}^3$, it has a velocity $\dot{\mathbf{x}}_i \in \mathbf{R}^3$, a mass $m_i \in \mathbf{R}$ and a momentum $\mathbf{p}_i = m_i \dot{\mathbf{x}}_i \in \mathbf{R}^3$, with $i \in [1,N]$. The masses m_i must satisfy the condition:

$$\sum_{i=1}^{N} m_i = m \tag{5}$$

where m is the total mass which must be a conserved quantity so that it follows:

$$\dot{\rho} + \rho \nabla \times \dot{\mathbf{x}}_B = 0 \tag{6}$$

where $\rho = dm/dV$ is the total mass density, with V total volume of the system and $\dot{\mathbf{x}}_B = \sum_{i=1}^{N} \boldsymbol{p}_i / m \in \mathbf{R}^3$, velocity of the centre of mass. The mass density must satisfy the following conservation law:

$$\dot{\rho}_i + \rho \nabla \times \dot{\mathbf{x}}_i = \rho \Xi \tag{7}$$

where ρ_i is the density of the ith elementary volume V_i, with $\sum_{i=1}^{N} V_i = V$, and Ξ is the source, generated by matter transfer, chemical reactions and thermodynamic transformations.

Inside this system, the principle of maximum entropy generation has been proved [3,7–9]: *in a general thermodynamic transformation, the condition of the stability for the open system steady states consists of the maximum of the entropy generation.*

3. Exergy and entropy generation

The exergy of a system is defined as the maximum shaft work that could be done by the composite of the system and a specified reference environment that is assumed to be infinite, in equilibrium, and ultimately to enclose all other systems: the environment is specified by stating its temperature, pressure and chemical composition.

The exergy was implicitly introduced [10] by Carnot in 1824 [11]; from this work Clapeyron [12], Rankine [13], Thomson [14] and Clausius [15] developed the Second Law of Thermodynamics, but it was Gibbs [16] to define the available energy, by introducing the available work, including the diffusion terms, even if also Tait and Lord Kelvin introduced a quantity similar to Gibbs availability [17] without any improvement on it [10]. The Gibbs results were developed by Duhem [18] and by Carathéodory [19], while, independently from Gibbs' results, Gouy [20,21] proved his useful energy theorem (today known as Gouy-Stodola theorem) and Stodola [22] used it in designing.

The results of Gouy were also applied by Jouget [23,24], Goodenough [25], DeBaufre [26], Born [27], Darrieus [28,29], Lerberghe and Glansdorff [30]. Maxwell [31] and Lorenz [32–35] developed some applications of the Gouy-Stodola theorem starting from the concept of entropy.

In the same years, Keenan [36–40], Bosnjakovic [41], Emden [42] and other physicists and engineers [10] developed and applied the concept of exergy.

Recently, the concept of exergy has been largely improved and used in different context by Wall [43–54] and Sciubba [55–62].

Exergy is not simply a thermodynamic property, but rather it is related to the reference environment [1]. Exergy is defined as the maximum amount of work which can be produced by a system or a flow of matter or energy as it comes to equilibrium with a reference environment. Exergy is a measure of the potential of the system or flow to cause changes, as a consequence of not being completely in stable equilibrium relative to the reference environment. Some properties are, here, summarized as follows, but they can be detailed in Refs. [1,9]:

1. a system in complete equilibrium with its environment does not have any exergy
2. the more a system deviates from the environment, the more exergy it carries
3. when the energy loses its quality, it results in exergy destroyed
4. an engineer designing a system is expected to aim for the highest possible technical efficiency at a minimum cost under

the prevailing technical, economic and legal conditions, but also with regard to ethical, ecological and social consequences. Exergy is a concept that makes this work a great deal easier

5. it is a primary tool in best addressing the impact of energy resource utilization on the environment
6. it is a suitable technique for furthering the goal of more efficient energy-resource use, for it enables the locations, types, and true magnitudes of wastes and losses to be determined
7. it is an efficient technique revealing whether or not and by how much it is possible to design more efficient energy systems by reducing the inefficiencies in existing systems
8. exergy is not subject to a conservation law.

Maximal possible conversion of heat Q to work W_t, known as exergy content of heat, depends on the temperature T at which heat is available and the temperature level T_a at which the reject heat can be disposed, that is the temperature of the surrounding. The upper limit for conversion is the Carnot efficiency 1—T_2/T_1, where T_1 and T_2 are, respectively, the higher and lower temperature of the transformation considered [9]. Consequently, exergy exchanged is defined as [9]:

$$B=\left(1-\frac{T_a}{T}\right)Q \tag{8}$$

Now, considering the relation (2), it follows:

$$S=\Delta S_e+S_g=\int\left(\frac{\delta Q}{T}\right)_{\text{rev}}=\int\frac{1}{T}d\left[\left(1-\frac{T_a}{T}\right)^{-1}B\right] \tag{9}$$

As a consequence of the principle of maximum entropy generation and considering that:

$$\begin{aligned}&\delta S_g=0\\&d(\Delta S_e)=0\end{aligned} \tag{10}$$

it follows that

$$\frac{1}{T}d\left[\left(1-\frac{T_a}{T}\right)^{-1}B\right]=0 \tag{11}$$

and

$$\frac{dB}{dT}=-\frac{T_a/T^2}{1-T_a/T}B \tag{12}$$

It follows that:

1. if $T>T_a$ then $dB/dT<0$ and $dB/d\tau$ represents the maximum power generated during the process;
2. if $T<T_a$ then $dB/dT>0$ and $dB/d\tau$ represents the minimum power required during the process.

From this result, exergy output is not balance the exergy input for real processes in open systems since a part of the exergy input is always destroyed according to the Second Law of Thermodynamics for real processes, as it is pointed out also by the entropy generation maximum principle. Moreover, exergy analysis and entropy generation analysis allow us to determine the most efficient process based on wasting and destroying as little available work as possible from a given input of available work.

4. Some applications

Exergy represents a new approach to efficiency and all the related subject. Indeed, when the efficiency of a process is studied it is possible to use two different approaches:

1. the first law analysis, known also as the net energy analysis: it allows to trace the energy flows useful to produce products or services. Its mathematical expression is the energy balance:

   $$\sum_{\text{in}}G_{\text{in}}(h+e_k+e_p)_{\text{in}}-\sum_{\text{out}}G_{\text{out}}(h+e_k+e_p)_{\text{out}}+\sum_i Q_i-W=0 \tag{13}$$

   where G is the mass flow, h is the specific enthalpy, e_k and e_p are the kinetic and the potential specific energy, Q is the exchanged heat and W is the work done. From this equation a useful formulation of the first law efficiency was proposed [63] as:

   $$\eta_{\text{I}}=\frac{H_{\text{us,out}}}{H_{\text{in}}} \tag{14}$$

   where $H_{\text{us,out}}$ represents the raw energy resource converted to useful energy, met downstream as final or end-use demand, while H_{in} is the input enthalpy
2. the second law analysis, known also as the entropy or the exergy analysis: this law allows to take into account the degradation of the energy due to irreversible processes. In relation to this analysis the exergy balance equation:

$$\sum_{\text{in}}G_{\text{in}}b_{\text{in}}-\sum_{\text{out}}G_{\text{out}}b_{\text{out}}+\sum_i(B_Q-B_W)_i-B_\lambda=0 \tag{15}$$

where G is the mass flow, b is the specific exergy, B_Q is the exergy associated with the exchanged heat Q, B_W is the exergy associated with the work done W and $B_\lambda=B_{\text{in}}-B_{\text{out}}$ is the exergy loss for irreversibility. From this equation a useful formulation of the second law efficiency was proposed [63] as:

$$\eta_{\text{II}}=\frac{B_{\text{out}}}{B_{\text{in}}} \tag{16}$$

First law analysis does not consider the energy quality, while the second law allows to point out that not all the heat input can be converted into useful work, because of the irreversibility. This law requires the definition of parameters that allows to quantify of the maximum amount of work achievable in a given system with different energy sources: this quantity is just the exergy B [56–61]. Consequently, it represents the thermodynamic quality of the energy of a system [63].

This approach has been successfully used [10] in:

1. steam power cycles
2. gas turbine cycles
3. renewable energy cycles
4. heat exchangers and heat networking
5. cryogenics
6. chemical processes
7. distillation and desalination
8. industrial and agricultural systems analysis
9. exergo-economics

In the following sections two examples of the use of exergy analysis will be developed, while for other applications many references can be found in [10].

4.1. *Fluid convection: Bénard cells*

In order to analyse a real example the fluid flow is described. Considering a fluid system for the small system, the system is identical to a convection system investigated by Bénard [64]. In this system, fluid is heated at the bottom and cooled at the top, and the resultant expansion and contraction lead to a top-heavy density distribution that is gravitationally unstable [65]. The potential energy in this top-heavy density distribution is generated by the differential heating and results from the conversion of the heat energy into work. When the temperature difference becomes larger than a certain critical value, the fluid is no longer stable against small perturbations, and convective motions tend to develop [65].

Once convection starts, the dynamic equation and conservation equations that govern the dynamics of the system become non linear, and this non- linearity makes the analytical solution difficult to obtain. Once convection starts, the fluid motion itself transports the heat energy, and thereby the total heat flux F increases. The generated potential energy in this case is converted into the kinetic energy of the fluid and then dissipated into heat energy by viscous dissipation. The conversion process is related to the non linear dynamic [65]. When the system can be seen to be in a steady state in a statistical sense, the generation rate of the potential energy has to be balanced by the viscous dissipation rate [65]. Then, the inflow rate of heat should be equal to the outflow rate. In this steady state the entropy generation S_g, in the time τ, is [66]:

$$S_g = \int_0^\tau dt \int_V \frac{1}{T}\left[\frac{\partial(\rho c T)}{\partial t} + \nabla \times (\rho c T \boldsymbol{v}) + p\nabla \times \boldsymbol{v} + \nabla \times \boldsymbol{F}\right] dV \qquad (17)$$

where ρ is the density of the fluid, c is the specific heat at constant volume, T is the absolute temperature, v is the velocity of the fluid, p is the pressure, V is the volume of the fluid system, A is the surface surrounding the system, and F is the heat flux at the surface, defined as positive outward. The transport of heat is caused by a movement of internal energy of fluid from one place to another, but it is essentially a reversible process. However, the heat transport, which consists of a movement of hot water into cold water, leads to a large local temperature gradient at the very front of the fluid, resulting in a considerable amount of entropy generation by the heat conduction at the front. This quantity is verified to be maximum [65]. Following the previous results, if a power system is considered, $T > T_a$ and $dB/d\tau = (T - T_a)\left(\dot{S}_e + \dot{S}_g\right)$ represents the maximum power generated during the process

4.2. Brayton magnetic cooling

The magnetocaloric effect, which is intrinsic to all magnetic materials, indicates that the paramagnetic or soft ferromagnetic materials expel heat and their magnetic entropy decreases when the magnetic field is applied isothermally; or otherwise absorb heat and their magnetic entropy increase when the magnetic field is reduced isothermally [67].

Important characteristics of a magnetic material are its total entropy S and the entropy of its magnetic subsystem S_M (magnetic entropy). Entropy can be changed by variation of the magnetic field, temperature and other thermodynamic parameters. The entropy of magnet at constant pressure, $S(T,H)$ is magnetic field and temperature dependent; it consists of the magnetic entropy $S_M(T,H)$, both magnetic field and temperature dependent, the lattice entropy $S_L(T)$ and the electronic entropy $S_E(T)$, both only temperature dependent [68]:

$$S(T,H) = S_M(T,H) + S_L(T) + S_E(T) \qquad (18)$$

Magnetic refrigerator completes cooling-refrigeration by magnetic material through magnetic refrigeration cycle. In general a magnetic refrigeration cycle consists of magnetization and demagnetization in which heat is expelled and absorbed, respectively, and two other benign middle processes.

In Fig. 1 the magnetic Brayton cycle is considered: it consists of two adiabatic processes and two isofield processes. The magnetic refrigerant cycles between the magnetic field of H_0 and H_1, and the temperature of high and low temperature heat source T_H and T_C, respectively. The total entropy and the magnetic part are displayed for an applied external field H_1 and H_0. During the isofield cooling process A→B (constant magnetic field of H_1), magnetic refrigerant expels heat of the area of AB14. During the isofield heating process C→D (constant magnetic field H_0), magnetic refrigerant absorbs heat of the area of DC14. No heat flows from and out of the magnetic refrigerant during the adiabatic magnetization process D→A and the adiabatic demagnetization B→C process. The Brayton cycle can exhibit optimal performance as well with magnetic refrigerants having parallel T–S curves [69]. Since the lattice entropy is too large to neglect in room temperature, part of the refrigeration capacity of the magnetic refrigerant is consumed for cooling the thermal load of lattice system, decreasing the gross cooling capacity of the magnetic refrigerant [70]. By adding a regenerator to the magnetic refrigeration system, the heat expelled by lattice system in one stage of the cycle is restored and returned to lattice system in another stage. So the capacity used for cooling lattice system load can be utilized effectively for the increase of effective entropy change and temperature span.

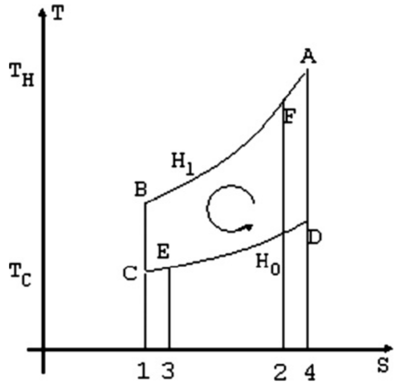

Fig. 1. Magnetic Brayton cycle.

The magnetic refrigeration ideal *COP* has recently been studied in [68] and it is usually defined as:

$$COP = \frac{Q_0}{W} \qquad (19)$$

with Q_0 the subtracted heat because of the magnetocaloric effect, and W the work done. It is useful to underline that only the magnetic entropy can be controlled by changing the strength of the magnetic field.

Some considerations have been introduced [67,68]:

1. magnetization at constant field in both paramagnets and ferromagnets decrease with increasing temperature $(\partial M/\partial T)_H < 0$
2. large total angular momentum number J and Land factor g of ferromagnetic material, are crucial to magnetocaloric effect
3. modest Debye temperature
4. modest Curie temperature in the vicinity of working temperature to guarantee that the large magnetic entropy change can be obtained in the whole temperature range of the cycle
5. essentially zero magnetic hysteresis
6. small specific heat and large thermal conductivity to ensure remarkable temperature change and rapid heat exchange
7. large electric resistance to avoid the eddy current loss
8. fine molding and processing behaviour to fabricate the magnetic materials satisfactory to the magnetic refrigeration
9. the *COP* depends on temperatures in non linear way
10. it does not depend from the value of the magnetic field, but only from its variation.

Since the lattice entropy is too large to be neglected in room temperature, part of the refrigeration capacity of the magnetic refrigerant is consumed for cooling the thermal load of lattice system, decreasing the gross cooling capacity of the magnetic refrigerant [70]. By adding a regenerator to the magnetic refrigeration system, the heat expelled by lattice system in one stage of the cycle is restored and returned to lattice system in another stage. So the capacity used for cooling lattice system load can be utilized effectively for the increase of effective entropy change and temperature span.

The magnetic Brayton cycle is considered as previously described. During the isofield cooling process A→B (constant magnetic field of H_1), magnetic refrigerant expels heat Q_1 equal to the area of AB14 in Fig. 1. During the isofield heating process C→D (constant magnetic field H_0), magnetic refrigerant absorbs heat Q_0 equal to the area of DC14. No heat flows from and out of the magnetic refrigerant during the adiabatic magnetization process D→A and the adiabatic demagnetization B→C process. To develop the exergy analysis of this cycle it is necessary to evaluate these areas, but to do so the function $S=S(T,H)$ must be known.

The heat exchanged is:

$$\begin{aligned} Q_0 &= -\int_A^B TdS = \text{area(DC14)} \\ Q_1 &= \int_C^D TdS = \text{area(AB14)} \end{aligned} \tag{20}$$

These integrals can be obtained by evaluating in a geometric way the two areas as:

$$\begin{aligned} Q_0 &= \text{area(DC14)} = \frac{T_C+T_D}{2}(S_D-S_C) \\ Q_1 &= \text{area(AB14)} = \frac{T_A+T_B}{2}(S_A-S_B) \end{aligned} \tag{21}$$

where $T_{1m}=(T_A+T_B)/2$ is the mean value of the temperature between T_A and T_B and $T_{0m}=(T_C+T_D)/2$ is the mean value of the temperature between T_C and T_D. Considering that $(S_A-S_B)=(S_D-S_C)=\Delta S$ then it follows:

$$\begin{aligned} Q_0 &= T_{0m}\Delta S \\ Q_1 &= T_{1m}\Delta S \end{aligned} \tag{22}$$

consequently, it follows:

$$\begin{aligned} B_0 &= \left(1-\frac{T_a}{T_{0m}}\right)Q_0 = \left(1-\frac{T_a}{T_{0m}}\right)T_{0m}\Delta S \\ B_1 &= \left(1-\frac{T_a}{T_{1m}}\right)Q_1 = \left(1-\frac{T_a}{T_{1m}}\right)T_{1m}\Delta S \\ W &= Q_1-Q_0 = (T_{1m}-T_{0m})\Delta S \\ COP &= \frac{Q_0}{W} = \frac{T_{0m}}{T_{1m}-T_{0m}} \\ \eta_{\text{ex}} &= \frac{B_0}{B_0+B_1} = \frac{T_{0m}-T_a}{T_{1m}+T_{0m}-2T_a} \end{aligned} \tag{23}$$

with η_{ex} exergy efficiency.

5. Conclusions

The entropy concept and its production in non-equilibrium processes form the basis of modern thermodynamics and statistical physics [7,71-73]. Entropy has been proved to be a quantity that is related to non-equilibrium dissipative processes. The second law of thermodynamics states that for an arbitrary adiabatic process the entropy of the final state is equal to (reversible process) or larger than that of the initial state, what means that the entropy tends to grow because of irreversibility.

Theoretical and mathematical physics study idealized systems and one of the open problems is the understanding of how real systems are related to their idealization. In phenomena out of equilibrium, irreversibility manifests itself because the fluctuations of the physical quantities, which bring the system apparently out of stationary states, but they occur symmetrically about their average values [2]. This quantity was related to the entropy generation.

In the last decades, the fundamental role of entropy generation has been pointed out in the analysis of real systems and an extremum principle for this quantity has been introduced [3]. Exergy analysis takes the entropy portion into consideration by including irreversibility [1].

In this paper a link between entropy generation and exergy has been summarized. It has been pointed out that, as a consequence of the maximum entropy generation, $dB/d\tau$ represents the maximum power generated during the process if $T>T_a$, while $dB/d\tau$ represents the minimum power required during the process if $T<T_a$. Entropy generation and exergy analysis of the open systems allow to obtain a measure of how far the open real systems deviate from equilibrium with their environment.

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