Thermodynamic Optimality criteria for biological systems in linear irreversible thermodynamics

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Abstract. In this paper the methodology of the so-called Linear Irreversible Thermodynamics (LIT) is applied; although traditionally used locally to study general systems in non-equilibrium states in which it is consider both internal and external contributions to the entropy increments in order to analyze the efficiency of two coupled processes with generalized fluxes $J_1, J_2$ and their corresponding forces $X_1, X_2$. We extend the former analysis to takes into account two different operating regimes namely: Omega Function and Efficient Power criterion, respectively. Results show analogies in the optimal performance between and we can say that there exist a criteria of optimization which can be used specially for biological systems where a good design of the biological parameters made by nature at maximum efficient power conditions lead to more efficient engines than those at the maximum power conditions or ecological conditions.

1. Introduction

It is well known that the universal validity of the Carnot efficiency $\eta_C = 1 - T_2/T_1 \equiv 1 - \tau$ for any reversible heat engine operating between reservoirs at temperatures $T_1$ and $T_2$ ($T_1 > T_2$) has little practical relevance since it applies to zero-power output heat devices. On the contrary, real heat engines work at nonzero power and evolve along irreversible paths coming from finite-time and finite-size unavoidable constraints. In 1975, Curzon and Ahlborn [1] introduced a Carnot-like thermal engine in which there was no thermal equilibrium between the working fluid and the thermal reservoirs at the isothermal branches of the cycle. Curzon and Ahlborn (CA) demonstrated that such an engine delivers nonzero power, a positive entropy production and has more realistic efficiency than that the Carnot engine. The efficiency of a CA engine in the performance of maximum power is given by $\eta_{CA} = 1 - \sqrt{T_2/T_1}$. We can thus conclude that the CA engine is a better approximation to real engines than the Carnot engine.

This seminal paper led to the establishment of a new brand of irreversible thermodynamics, known as finite-time thermodynamics (FTT), which has been developed during last decades [2–11]. One of central
questions addressed in FTT is to identify optimal procedures for different objective functions. Originally Curzon and Ahlborn proposed to optimize the power output but some other different functions had been proposed. Besides, most of energy-transfer devices discussed by the FTT were heat engines although, some optimal performance analyses were also conducted where biochemical reaction models were analyzed [12–14].

For instance, Angulo-Brown et al. [15] proposed that the two ways of producing ATP follow different criteria of thermodynamic optimization. The anaerobic glycolysis is carried out by a chemical reaction maximizing power output, while respiration undergoes a process whose optimized thermodynamic function is that representing the best compromise between high power output and low entropy production [16]. Previously, Stucki et. al. [17] analyzed, with the aid of Caplan and Essig’s definitions of power output and efficiency [12], some optimum working regimes different from that of minimum entropy production studied before by Prigogine [18].

In the present work we extend the former analysis to takes into account two different operating regimes namely: Omega Function and Efficient Power criterion, respectively. For the first case; the Omega Function, this feature was proposed based on a unified optimization criterion [19] which represents the best compromise between the benefits and losses of energy to any device and has the advantage that it does not explicitly require the entropy expression to be applied, or any other environmental parameter, such as the case where the Exergy or the Ecological criteria are used as objective functions [20]. The second maximization of this function provides a compromise between power and efficiency, where the designed parameters at maximum efficient power conditions lead to more efficient engines than those at the maximum power conditions [21]. Finally, the advantages and disadvantages of the mentioned regimes are discussed from a thermodynamical point of view.

2. Linear irreversible thermodynamics and optimal regimes

Let us consider, following Prigogine [18] and Yourgrau et al. [22], a system in a steady state consisting of two coupled processes with generalized fluxes $J_1, J_2$ and their corresponding forces $X_1, X_2$. As is well known from the theories of near-equilibrium irreversible thermodynamics, the system’s entropy production rate is given by,

$$\sigma = J_1 X_1 + J_2 X_2 \quad \cdots (1)$$

Without loss of generality, we can choose $J_1 X_1 > 0$ to be the driven process, and $J_2 X_2 < 0$ to be the driver process [12]. Obviously $J_1 X_1 + J_2 X_2 > 0$, in accordance with the second law of thermodynamics. To have a steady state, we shall consider $X_2$ constant [12, 22]. Although steady states can also be obtained by setting $J_2$ or $J_2 X_2$ constant [12], $X_2$ constant seems to be the case in many biological systems [12,18]. Caplan and Essig [12] introduced definitions of power output $P$ and efficiency $\eta$ for energy converters working in steady states at constant pressure and temperature, in the following manner:

$$P = -T J_1 X_1 \quad \cdots (2)$$

and

$$\eta = -\frac{J_1 X_1}{J_2 X_2} \quad \cdots (3)$$
With the above definitions, optimum regimes like those which maximize the Omega Function and Efficient Power criterion, and in general optimize proper functions of these variables, can be studied. It is important to notice that although we take the optimum performance regimes usually studied by Finite Time Thermodynamics (FTT), the approaches of this theory and Linear Irreversible Thermodynamics (LIT) (the one here employed), are quite different. FTT studies thermal engines working in cycles and considers them as internally reversible taking into account only external contributions to the system’s entropy increments. On the other hand, LIT locally studies general systems in non-equilibrium states and considers both internal and external contributions to the entropy increments. In the present work we consider only internal irreversibilities since they are responsible for the whole entropy increments of the universe. Although in general both theories led to similar results as regards the thermodynamically characteristics of the performance regimes studied.

For linear energy converters the relations between fluxes and forces, or phenomenological relations, are as follows [12, 23-26]:

\[ J_i = \sum_{j=1}^{2} L_{ij} X_j \quad i = 1,2 \quad \text{(4)} \]

with constants \( L_{ij} \) called the phenomenological coefficients. It is also assumed the validity of Onsager’s reciprocity theorem which establishes the symmetry of the matrix of phenomenological coefficients, i.e. \( L_{ij} = L_{ji} \).

From equation (4) and Onsager’s reciprocity theorem, equations (1)-(3) become;

\[ \sigma = L_{22} X_2^2 \left[ (1 - q^2) + q^2 (1 - x)^2 \right] \quad \text{(5)} \]

\[ P = TL_{22} X_2^2 q^2 x (1 - x) \quad \text{(6)} \]

\[ \eta = -\frac{q^2 x (1-x)}{1-q^2 x} \quad \text{(7)} \]

with \( q = \frac{L_{12}}{L_{11} L_{22}} \) a coefficient that measures the degree of coupling between the driver and the driven process [12], \( x = \frac{X_1}{X_1^0} \) and \( X_1^0 = -\left(\frac{L_{12}}{L_{11}}\right) X_2^0 \), the driven force at which \( J_1 = 0 \).

Now the behavior for the Omega function is presented, as we mention later the Omega function was proposed based on a unified optimization criterion [19] which represents the best compromise between the benefits and losses of energy to any device and has the advantage that it does not explicitly require the entropy expression to be applied, it is given by,

\[ \Omega = \frac{2\eta - 1}{\eta} W_{\text{out}} \quad \text{(8)} \]

Substituting equations (6) and (7) into equation (8) yields,

\[ \Omega = -TL_{22} X_2^2 \left[ (1 - q^2 x) \left( -1 + \frac{2q^2 (1-x) x}{1-q^2 x} \right) \right] \quad \text{(9)} \]
For the analysis $x$ is taken as the independent variable, and in order to obtain the maximum Omega function what must be solved is the following equation $\frac{\partial \Omega}{\partial x} = 0$. Then from equation (9) the condition for the $\Omega$ function to be maximum is $x = 0.75$. Now, substituting the maximum value of $x = 0.75$ into equation (7) and performing a series expansion of this efficiency in terms of $q$ value around 0, we obtain, for instance, the expression for efficiency at maximum Omega Function given by,

$$\eta_\Omega = 0.1875 q^2 + 0.140625 q^4 + 0.105469 q^6 + 0.0791016 q^8 + 0(x^{10}) \ldots (10)$$

In the other hand, the behavior of the under maximum efficient power regime will also be discussed. This approach was recently proposed by Yilmaz [21] in the context of heat thermal engines, and is defined as the product of the power output and efficiency, which states:

$$P_E = \eta W_{out} \ldots \ldots \ldots \ldots (11)$$

Substituting equations (6) and (7) in equation (11) yields,

$$P_E = -TL_{22}x^2 \left[ \frac{q^4(1-x)^2x^2}{1-q^2x_0} \right] \ldots \ldots \ldots (12)$$

For the analysis $x$ is taken as the independent variable, and in order to obtain the maximum efficient power what must be solved is the following equation $\frac{\partial P_E}{\partial x} = 0$. Then, from equation (12) the condition for the $P_E$ function to be maximum is,

$$x = \frac{4+q^2-\sqrt{16-16q^2+q^4}}{6q^2} \ldots \ldots \ldots (13)$$

Now, substituting the maximum value of $x$ into equation (7) and performing a series expansion of this efficiency in terms of $q$ value around 0, we obtain, for instance, the expression for efficiency at maximum $P_E$ function given by,

$$\eta_{P_E} = q^2/4 + q^4/8 + 19q^6/256 + 25q^8/512 + 0(x^{10}) \ldots (14)$$

Fig. 1 presents optimized efficiency under the two criteria as a function of $q$, also maximum efficiency is shown. The figure shows that values of efficiency operating under maximum Omega criterion are greater with respect to the Maximum Efficient Power, until $q = 0.9$, where the behavior changes and form this value until $q = 1.0$ the values of efficiency operating under maximum Omega criterion are lesser with respect to the Maximum Efficient Power.
Figure 1. Efficiency under the two thermodynamic optimization criteria as a function of $q$, the Maximum Efficient Power represented by the dotted line and Omega Function the continuous line.

Figure 2 presents optimized efficiency under the four criteria as a function of $q$, the figure shows that values of efficiency operating under maximum Omega criterion (continuous), Maximum Power [14] (blue dashed), Maximum Ecological [14] (also continuous line overprint with Omega), and Function Maximum Efficient Power (dashed).

Figure 2. Efficiency under four thermodynamic optimization criteria as a function of $q$, namely, at Maximum Efficient Power, in the Omega Function, Ecological Function and in the Maximum Power function.

3. Concluding Remarks

In this paper the methodology of the so-called LIT is applied; although traditionally used locally to study general systems in non-equilibrium states in which it is consider both internal and external contributions to the entropy increments in order to analyze the efficiency of two coupled processes with generalized fluxes $J_1, J_2$ and their corresponding forces $X_1, X_2$. We extend the former analysis to takes into account two different operating regimes namely: Omega Function and Efficient Power criterion, respectively.

The behavior of the efficiency as a function of $q$ is shown for the Omega and the Efficient Power functions, respectively in Figure 1. From the above analysis, it can be shown that there exists a
characteristic value of \( x \) that maximizes these functions. Besides, when we obtain the efficiency in terms of the phenomenological coefficient \( q \) for both objective functions (equations 14 and 10), it seems a convex function for which the efficiency is greater when \( q \) grows.

When these two functions are compared with those obtained by Santillán et al. [14] depicted in Figure 2 (Efficiency at Maximum Power and Efficiency and Maximum Ecological Function), it is shown that for \( q \) close to one, the efficiency operating under the Efficient Power function is greater than the other three (Omega function, Maximum Power and Ecological function). Also, it is worth to notice that both the Omega function and the Ecological function have the same behavior, which is a characteristic of the isothermally of the system.

Finally, from the above we can say that there exist a criteria of optimization which can be used specially for biological systems where a good design of the biological parameters made by nature at maximum efficient power conditions lead to more efficient engines than those at the maximum power conditions or ecological conditions (where the main considerations are energetic), this suggest some differences between biological systems based on its own design.

4. References

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