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Generalization of exergy analysis

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HIGHLIGHTS

- The area of validity of standard exergy analysis is discussed carefully.
- A generalization of exergy analysis is developed within classical irreversible thermodynamics.
- The generalization is demonstrated on fuel cells, osmotic power plants and heat engines.
- A rigorous method indicating where exactly in a device useful work is being lost is developed.
- A general algorithm of thermodynamic optimization is formulated.

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ABSTRACT

Exergy analysis, which provides means of calculating efficiency losses in industrial devices, is reviewed, and the area of its validity is carefully discussed. Consequently, a generalization is proposed, which holds also beyond the area of applicability of exergy analysis. The generalization is formulated within the framework of classical irreversible thermodynamics, and interestingly it leads to minimization of a functional different from entropy production. Fuel cells, osmotic power plants and heat engines are analyzed within the theory. In particular, the theory is demonstrated on a toy model of solid oxide fuel cells quantitatively. Eventually, a new general algorithm of thermodynamic optimization is proposed.

1. Introduction

Consider a device producing useful work, e.g. electricity, which is in a steady state, i.e. its thermodynamic state is not varying in time. It is difficult to overestimate importance of the two following questions:

1. What is the maximum work possibly produced by the device?
2. The actual work is lower than the maximum work. Where exactly in the device is the work being lost and how much exactly at each point of the device?

An answer to the first question provides a measure of how efficient the device is. An answer to the second question identifies parts of the device that should be enhanced.

Answers to those two questions may seem to be provided by standard exergy analysis presented for example in [1–4], which has become a widely used tool among engineers. See [5–10] for solid oxide fuel cell (SOFC) applications, [11,12] for polymer-electrolyte membrane fuel cell (PEMFC) applications, [13] for applications in heat transfer, [14–16] for application in photovoltaics, [17] for cogeneration plants, [18] for studying the potential of natural gas for widespread use in transportation, [19] for a novel water desalination study, [20] for an interesting application of genetic algorithms and neural networks or [21] for a recent review of the Extended Exergy Accounting method and examples therein. Perhaps the closest optimization theory to the theory developed in this manuscript is given by endoreversible thermodynamics [22,23], which uses a similar approach to studying irreversible processes, namely their efficiency and various measures of performance. In this approach, a non-equilibrium system is described as a collection of equilibrium subsystems such that all the dissipative processes occur due to interaction between those subsystems. The finite number of subsystems typically yields analytical

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solutions in many real-world applications and high tractability of many stationary, periodic but also dynamic systems. Our approach, on the other hand, is based on local equilibrium assumption, that is adopted in classical irreversible thermodynamics, offering continuous modelling including computation of map of losses (see below).

What is new in this article?

- In this manuscript we show that the standard way exergy analysis is used (for example in SOFC modeling) is not general and predicts incorrect results in some cases since some assumptions inherently incorporated into exergy analysis may not be met. In other words, a new critical view of exergy analysis is presented and the method of optimization based on exergy analysis is generalized. The generalization is demonstrated on a toy model for SOFC in Section 5. In view of the above mentioned endoreversible thermodynamics it could be said that minimization of entropy production is not always an appropriate measure of performance when interested in measuring the maximal useful work.
- It is discussed that osmotic power plant is an example of such a situation in which exergy does not yield correct results. Hence, the standard definition and evaluation of plant efficiency is revised and a new algorithm of optimization is proposed.
- All the theory in this manuscript is based on non-equilibrium thermodynamics, and in order to derive the results consistently, it was necessary to reformulate some parts of the theory. In particular, electric potential of ions and electrons is identified with corresponding electrochemical potentials in 3 in order to overcome difficulties regarding electric potentials mentioned in [24]. Moreover, Butler–Volmer equation, which describes rates of electrochemical reactions, is formulated within non-equilibrium thermodynamic framework GENERIC with dissipation potential so that it can be consistently incorporated into the proposed optimization algorithm.

2. Standard exergy analysis

In this section we briefly review some results of standard exergy analysis which can be found for example in the following works: [1,25,2,26,27]. Although this section mainly reviews known facts, it is important to include it so that we are able to compare the new theory with the standard theory efficiently.

2.1. Steady state

Let us consider a device in a steady state. The device is in contact with reservoirs of both heat and matter and the device produces useful work (e.g. electricity). Exergy analysis provides answers to the questions what is the maximum possible useful work and where exactly the useful work is being lost. There is, however, an assumption inherently incorporated into exergy analysis which restricts validity of the theory to some extent. The assumption is identified later in this section and a generalization of exergy analysis free of the assumption is then proposed in Section 4.

A very precise formulation of exergy analysis was given by Adrian Bejan [1], where also the enormous importance of exergy analysis was discussed. Let us briefly recapitulate the main results. Consider a device in thermal contact with environments $0\dots n$, see Fig. 1 for illustration, and assume that the device is in a steady state. Besides heat transfer also mass transfer occurs at boundaries of the device.

Balance equations of energy and entropy of the device in a steady state can be written as

$$0 = \frac{dE}{dt} = \sum_{i=0}^{n} \Delta Q^i - \Delta W - \int_{\partial V} \sum_{\alpha} (h_\alpha + \varphi_\alpha)\mathbf{j}_\alpha \cdot d\mathbf{S} + \Delta KE \tag{1}$$

$$0 = \frac{dS}{dt} = \sum_{i=0}^{n} \frac{\Delta Q^i}{T^i} - \int_{\partial V} \sum_{\alpha} s_\alpha \mathbf{j}_\alpha \cdot d\mathbf{S} + d_{irr}S \tag{2}$$

where ΔW denotes steady state useful work being produced by the device, i.e. energy leaving the device per unit of time. φ_α denotes potential energy of species α, $\mathbf{j}_\alpha$ is mass flux of species α and ΔQ^i denotes conductive heat flux from the i-th environment into the device, e.g. transmitted by phonons. ΔKE denotes flux of kinetic energy into the device. Finally, s_α denotes partial specific entropy of species α, h_α stands for partial specific enthalpy of the species, see also (16), and $d_{irr}S$ is total entropy production in the device, i.e.

$$d_{irr}S = \int_V \sigma_s \, dV \tag{3}$$

with σ_s being entropy production density, which can be evaluated at each point of the device. Eliminating ΔQ^0 from balance of energy (1) and balance of entropy (2), a formula for useful work is obtained

$$\Delta W = \underbrace{\sum_{i=1}^{n}\left(1 - \frac{T^0}{T^i}\right)\Delta Q^i}_{\text{heat exergy}} \underbrace{- \int_{\partial V} \sum_{\alpha} (h_\alpha + \varphi_\alpha - T^0 s_\alpha)\mathbf{j}_\alpha \cdot d\mathbf{S} + \Delta KE}_{\text{flow exergy}} \underbrace{- T^0 d_{irr}S}_{\text{exergy destruction}} \tag{4}$$

From the second law of thermodynamics, which can be formulated in the sense that entropy production is non-negative, it follows that the maximum work one can obtain from the device is given by this last equation with $d_{irr}S$ equal to zero. That means that the maximum useful work is a function of the following quantities

$$\Delta W_{max}\left(\Delta Q^1, \dots, \Delta Q^n, \int_{\partial V} \sum_{\alpha} (h_\alpha + \varphi_\alpha - T^0 s_\alpha)\mathbf{j}_\alpha \cdot d\mathbf{S}, \Delta KE\right). \tag{5}$$

Thus, it is a function of all energy fluxes through the boundary except for ΔQ^0. Therefore, we can draw the conclusion that exergy analysis gives the maximum useful work one can obtain from a device when heat flux from the environment with temperature T^0 is not well controlled and when it is simultaneously the only not well controlled energy flux through the boundary of the device. Indeed, heat flux ΔQ^0 is the only energy flux through the boundary of the device which is not present in the final formula for maximum work (5).

The assumption that only ΔQ^0 is not known is important since it restricts validity of exergy analysis for example in fuel cells with non-isothermal boundary, which is shown in the next section.

On the other hand, if exergy analysis is applicable to the device, entropy production density σ_s evaluated at a point gives the amount of useful work which is being lost at the point. This means that plotting σ_s at each point of the device provides a map of losses which tells where exactly the useful work is being lost and thus identifies places where optimization can be done. This provides a very useful tool for efficient design of industrial devices, see for example [25,26].

Note that if the boundary of the device is isothermal, i.e. there is only heat reservoir with temperature T^0, the formula for useful work (4) simplifies to

$$\Delta W = \Delta G - T^0 \int_V \sigma_s \, dV \tag{6}$$

if kinetic and potential energies can be neglected. ΔG denotes steady flux of Gibbs energy of neutral species into the device

$$\Delta G = -\int_{\partial V} \sum_{\alpha \in n} \mu_\alpha \mathbf{j}_\alpha \cdot d\mathbf{S} \tag{7}$$