Chapter 2
Exergy, Exergy Costing, and Renewability
Analysis of Energy Conversion Processes

Symbols

\( B \) Exergy (kJ)
\( B \) Exergy rate/flow rate (kW)
\( b \) Specific exergy (kJ/kg)
\( B_{\text{emissions}} \) Exergy rate of wastes that are not treated or deactivated (kW)
\( B_{\text{destroyed}} \) Destroyed exergy rate (kW)
\( B_{\text{deactivation}} \) Destroyed exergy rate of additional natural resources during waste de-activation (kW)
\( B_{\text{disposal}} \) Exergy rate or flow rate related to waste disposal of the process (kW)
\( B_{\text{fossil}} \) Non-renewable exergy rate consumed on production processes chain (kW)
\( B_{\text{nat,res}} \) Exergy rate of the natural resources consumed by the processes (kW)
\( B_{\text{processing}} \) Exergy rate or flow rate required for extraction and preparation of the natural resources (kW)
\( B_{\text{product}} \) Exergy rate or flow rate associated to the products and byproducts/ useful effect (kW)
\( B_{\text{reject}} \) Exergy rate or flow rate of the rejects (kW)
\( B_{\text{utilities}} \) Exergy rate or flow rate required by the utilities of the process (kW)
\( C \) Cost ($)
\( C \) Cost rate ($/s)
\( c \) Specific heat, J/(kg K), specific cost (kJ/J, $/kJ, $/kg)
\( c_p \) Specific heat at constant pressure, J/(kgK)
\( C_{\text{eq}}, C_{\text{r}} \) Equipment cost of a given capacity ($); Equipment cost of a reference capacity ($)
\( E \) Energy (kJ)
\( E \) Energy rate/flow rate (kW)
\( f_{\text{O&M}} \) Annual operational and maintenance factor
\( f_a \) Capital recovery factor
\( g \) Gravitational acceleration (9.8 m/s\(^2\)); molar Gibbs free energy of formation (kJ/kmol)
\( \Delta G_0 \) Gibbs free energy variation in the direction of a given chemical reaction (kJ/kmol)

\( H; h \) Enthalpy flow rate (kW); specific enthalpy (kJ/kg)

HR Enthalpy of reactants (kJ/kmol)

HP Enthalpy of products (kJ/kmol)

\( I_e \) Energy investment (kJ)

\( I_{VC} \) Investment rate of equipment inside control volume ($/h, $/s)

\( i \) Interest rate (%)

LHV Lower heating value (kJ/kg)

\( m \) Mass flow rate (kg/s)

\( N \) Capital recovery period, operating time (year)

\( N_i \) Number of moles of species \( i \)

\( Q; q \) Heat rate (kW); heat rate per unit of mass flow rate (kJ/kg)

\( P \) Pressure (kPa)

\( R, \bar{R} \) Ideal gas constant (kJ/kg K), universal gas constant (kJ/kmol K)

\( S; s \) Entropy rate/flow rate (kW/K); specific entropy (kJ/kg K)

\( S, S_r \) Component size, component reference size (see Table 2.8)

\( S_{ger}, s_{ger} \) Entropy generation rate (kW/K); entropy generation rate per unit of mass flow rate (kJ/kg K)

\( T \) Temperature (\( ^\circ \text{C, K} \))

\( U; u \) Specific internal energy (kJ/kg), internal energy (kJ)

\( v \) Specific volume (m\(^3\)/kg); value scale

\( V \) Volume (m\(^3\))

\( W; w \) Power (kW); power per unit of mass flow rate (kJ/kg)

\( x \) Mole or mass fraction

\( z \) Elevation (m)

**Greek symbols**

\( \alpha \) Angle in Fig. 2.11, percent excess air, exponent of Eq. 2.84

\( \gamma_i \) Activity coefficient of species \( i \)

\( \Delta_{comb} \) Ratio between destroyed exergy and reactants exergy

\( \eta \) Efficiency

\( \theta \) Carnot factor

\( \lambda \) Renewability exergy index

\( \mu_i \) Chemical potential of species \( i \) (J/mol)

\( \nu \) Stoichiometric coefficient

\( v \) Velocity (m/s)

\( \varphi \) Ratio between chemical exergy and lower heating value

**Superscripts**

- Molar
- * Restricted reference state

s System
### Subscripts

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2.1 Exergy, Quality, and Efficiency

The concern with efficiency and quality of energy conversion processes is already present in the beginnings of the development of thermal engines. Biot in his Traité de Physique Expérimentale et Mathématique, Tome 4 Chap. VI [1, 10], draw attention to the following aspects:

Le plus important est la détermination de la temperature à laquelle il est le plus convenable d’employer la vapeur. En effet, plus elle est chaude, plus sa force élastique est considérable, et par conséquent plus elle produit d’effort sur la surface du piston qu’elle presse, le vide étant toujours de l’autre côté. Mais aussi il faut consommer plus de charbon pour produire une vapeur plus chaude; en sorte que le profit ou le désavantage de la température est un element à determiner.

This paragraph highlights the dependence of the performance of a heat engine with the fuel consumption and with the temperature level at which steam is generated, in other words, with the thermodynamic quality of steam.

The concept of exergy has its origin in the formulation presented by Gouy [6] and Stodola [18] which shows that the maximum potential for a system to perform work is a function of its internal energy and the ambient conditions (pressure, temperature, and composition). This concept was improved throughout the twentieth century by several authors, as indicated by Rivero [16] and showed in Table 2.1, where some exergy and related concepts are presented.

The search for thermodynamic quality standards is one of the most interesting challenges of the Engineering Thermodynamics. In the last decades, this concern is no more restricted to the performance quantification of a given process or equipment, but it extends to all the boundaries of any energy conversion process, including its energy inputs and wastes. This implies that, for every process and equipment and a given output:

- a larger energy input utilization as smaller is the conversion efficiency, and,
- a larger quantity of wastes, and consequently a higher potential to generate environmental impacts, as smaller is the conversion efficiency.

Although fundamental in the quantification of the terms of the efficiency expression, the energy balance, or the First Law of Thermodynamics, as well as, the concept of energy, are not enough to identify and correctly quantify what is usually
called inefficiencies. What is called inefficiency is a consequence of the occurrence of an irreversible process, in which there is entropy generation, for instance, the head loss in an isolated duct, where enthalpy is conserved and entropy increases provoked by an irreversible process: conversion of the work flow into internal energy.

In this sense, the use of the entropy balance, or the Second Law of Thermodynamics as complementary information to the energy balance, is of fundamental importance to quantify and to well understand the inefficiencies of energy conversion processes, the cost formation process of the products and wastes.

As discussed by Moore [11], the efficiencies of some systems and equipment are limited by restrictions imposed by the Second Law of Thermodynamics. These limits exist, for example, in conversions of:

- heat into work, as it happens in a heat engine;
- internal energy/enthalpy variation into work (turbine);
- chemical energy into work (fuel cell);
- chemical energy into kinetic energy (rocket);

Or, as characterized by Kotas [8], the conversion of ordered energy (work, kinetic energy, and potential energy) into disordered energy (internal energy, heat, and chemical energy) can be accomplished completely, but the inversion of these processes are always limited by the Second Law of Thermodynamics and the properties of the environment \((P_0, T_0, \mu_0)\) in which the system is placed.

### 2.2 Exergy and Exergy Balance

#### 2.2.1 Reversible Work

The concept of exergy can be introduced by using the concept of reversible work. It can also be shown that the so-called exergy balance is merely a linear
combination of the entropy and energy balances. These developments will be presented here for a simple case of processes that take place, in steady state, in a control volume with one inlet and one outlet, and neglecting the kinetic, potential, as well as electric, and magnetic effects, as represented in Fig. 2.1.

Equations 2.1 and 2.2 present the energy and entropy balances, per unit of mass flow rates that cross the boundaries at ‘i’ (inlet) and ‘e’ (outlet).

\[ q = h_e - h_i + w \]  \hspace{1cm} (2.1)

\[ s_e - s_i = \int \frac{\delta q}{T} + s_{ger} \]  \hspace{1cm} (2.2)

For the chosen control volume, one could ask the following question: ‘What is the maximum work that can be performed giving the same thermodynamic states at the inlet and outlet sections of the control volume?’ This maximum work is determined under the following conditions:

- all the processes within the control volume are reversible;
- the maximum work that can be generated using the heat rejected by the control volume is the one obtained from a Carnot engine, operating between temperatures \( T_i \) and \( T_e \) and the environment temperature where the control volume is placed (\( T_0 \)).

The determination of the maximum work is done, by considering another control volume which contains the preceding control volume and the Carnot engine. This new control volume is crossed by the same mass flow rates, and \( q_0 \) is the rejected heat of the Carnot engine. The energy and entropy balances for this new control volume are given by Eqs. 2.3 and 2.4:

\[ q_0 = h_e - h_i + w_{\text{max}} \]  \hspace{1cm} (2.3)

\[ s_e - s_i = q_0 / T_0 \]  \hspace{1cm} (2.4)

Substituting \( q_0 \) by \( (s_e - s_i)T_0 \), one obtains:

\[ w_{\text{max}} = h_i - h_e - T_0(s_i - s_e) \]  \hspace{1cm} (2.5)
Or, the term \([h_i - h_e - T_0(s_i - s_e)]\) characterizes a maximum potential to perform work giving the states ‘i’ and ‘e’.

This development could be done for the original condition where there are irreversible processes inside the control volume as well as the original values of \(w\) and \(q\). In this case, the maximum work could be obtained in a similar way: including a Carnot engine that operates by using \(q\) and rejecting \(q'_0\) to the environment.

For the reversible engine, it can be written:

\[
\oint \frac{\delta Q}{T} = 0 = \int_{T_i}^{T_e} \left( \frac{\delta q}{T} \right) + \int \left( \frac{\delta q'_0}{T_0} \right) \tag{2.6}
\]

And, by taking this expression into the entropy balance for the original control volume with the Carnot engine, one gets:

\[
s_e - s_i = q_0/T_0 + s_{ger} \tag{2.7}
\]

Also, it is possible to write the energy balance for the region that encompasses the reversible engine and the original control volume:

\[
q'_0 = h_e - h_i + w + w_{mr} \tag{2.8}
\]

In Eq. 2.8 the specific work of the Carnot engine, taking into account that heat has different signs for the heat engine control volume, is

\[
w_{mr} = q - q'_0 \tag{2.9}
\]

By substituting \(q'_0\) and \(w_{mr}\), one gets:

\[
T_0(s_e - s_i) - T_0 s_{ger} = h_e - h_i + w + q\eta_{mr} \tag{2.10}
\]

where

\[
w_{mr} = q\eta_{mr} \tag{2.11}
\]

In this way, Eq. 2.10 can be written giving:

\[
h_i - h_e - T_0(s_i - s_e) = w + q\eta_{mr} + T_0 s_{ger}
\]

with:

\[
\eta_{mr} = 1 - \frac{T_0}{q} \int_{T_i}^{T_e} \left( \frac{\delta q}{T} \right) \tag{2.12}
\]

It is evident that, as shown by Eq. 2.5, the term \([h_i - h_e - T_0(s_i - s_e)]\) also characterizes a potential for doing work that in the occurrence of irreversible processes is reduced by the product \(T_0s_{ger}\), or the so-called irreversibility. Eventually, this potential is completed destroyed, or:
This scenario happens in dissipative processes, for instance, during the flow through an expansion valve where: \( h_i = h_e, w = 0, q = 0 \) and \( s_{\text{ger}} > 0 \).

### 2.2.2 Exergy and Exergy Balance

Equation 2.10 can simply be obtained by multiplying the entropy balance by \(-T_0\) and adding this equation to the energy balance. The result, a linear combination of the entropy and energy balances, gives:

\[
[h_i - h_e - T_0(s_i - s_e)] = w + q \int_{T_i}^{T_e} \left( \frac{\delta q}{T} \right) + T_0 s_{\text{ger}} \tag{2.14}
\]

In the case where all processes inside the control volume are reversible, the control volume interacts only with the environment, and the mass flow rate at the outlet section is in thermodynamic equilibrium with the environment \((h = h_0\) and \(s = s_0)\). Eq. 2.14 becomes the expression of the maximum reversible work associated to the inlet flow rate state of the control volume:

\[
[h_i - h_e - T_0(s_i - s_e)] = w + q \int_{T_i}^{T_e} \left( \frac{\delta q}{T} \right) = w_{\text{max}} \tag{2.15}
\]

This maximum reversible work is called specific exergy of the flow rate at the inlet section of the control volume:

\[
b = [h_i - h_0 - T_0(s_i - s_0)] \tag{2.16}
\]

It is worth to note that the specific exergy is a function of properties of two thermodynamic states: the state in which the mass flow rate is and the state where this mass flow rate would be in thermodynamic equilibrium with the environment components. In that sense, the specific exergy is a special thermodynamic property, function of two thermodynamic states, and its value gives the maximum potential for doing work.

For a general situation, as shown in Fig. 2.2, where there are several inlet and outlet sections, heat exchanges at temperatures \(T_j\), unsteady state regime and deformable control volume, the linear combination of the energy and entropy balances, gives:

\[
\frac{d}{dt}(E + P_0 V - T_0 S) = \frac{dB}{dt} = \sum_j \left( 1 - \frac{T_0}{T_j} \right) Q_j - W_{\text{ef}} + \sum_i m_i(h_i - T_0 s_i)
\]

\[
- \sum_{c} m_c(h_c - T_0 s_c) - T_0 S_{\text{ger}} \tag{2.17}
\]
This equation, called the exergy balance, is composed of the following terms:

\[
\frac{d}{dt}(E + P_0V - T_0S) = \frac{dB}{dt} : \text{control volume exergy variation rate}
\]

\[
\sum_i H_i - \sum_e H_e - T_0(\sum_i S_i - \sum_e S_e) : \text{exergy flow rate variation between inlet and outlet control volume sections.}
\]

\[
B_Q = Q_j(1 - T_0/T_j) : \text{exergy rate associated to heat transfer rate (maximum work that could be performed by a Carnot engine operating between } T_j \text{ and } T_0, \text{ receiving } Q_j \text{ at } T_j, \text{ and rejecting heat to the environment at } T_0).\]

\[
W_{ef} = \text{pure exergy rate: effective work rate performed or received by the control volume.}
\]

\[
B_{dest} = T_0S_{ger} : \text{destroyed exergy rate or irreversibility rate (rate of available work destroyed due to irreversible processes that take place inside the control volume).}
\]

Equation 2.17 can be considered as the law of energy degrading because it allows quantifying the reduction of the work capacity of a given energy conversion process (or processes) caused by the occurrence of irreversible processes.

As a consequence it is possible to conclude that the capacity for doing work (exergy) is not conservative, being always reduced every time that any irreversible process happens inside the analyzed control volume, such as non resisted expansion, head loss, mixture, heat transfer, and chemical reaction.

Neglecting nuclear, magnetic, electric, and surface tension effects, one can divide the exergy in four components: kinetic, potential, physical, and chemical, as shown in Fig. 2.3 and Eq. 2.18.

\[
b = b_{\text{kin}} + b_{\text{pot}} + b_{\text{ph}} + b_{\text{ch}}
\]
Kinetic and potential exergy correspond, respectively, to kinetic and potential energy, because both energy forms can be completely converted into work:

\[ b_{\text{kin}} = \frac{v^2}{2} \]  
\[ b_{\text{pot}} = g\zeta \]  

Physical exergy is equivalent to the maximum work that can be performed when a system or a flow rate moves from a given thermodynamic state to the restricted reference state (indicated as *) where it is in thermal and mechanical equilibrium with the environment. For a system, the physical exergy is given by:

\[ b^s = u - u^* + P_0(v - v^*) - T_0(s - s^*) \]  

And for a mass flow rate:

\[ b = h - h^* - T_0(s - s^*) \]  

It is important to notice that the term \( P_0(v - v^*) \) that appears in Eq. 2.21 is a non-available work that the system performs, or receives, due to its interaction with atmospheric pressure.

For a perfect gas, with constant pressure specific heat, \( c_p \), the expression of the physical exergy is:

\[ b_{\text{ph}} = c_p \left[ (T - T_0) - T_0 \ln \left( \frac{T}{T_0} \right) \right] + RT_0 \ln \left( \frac{P}{P_0} \right) \]  

For solids and liquids, when the behavior of incompressible substance can be assumed, the physical exergy is done, by Eq. 2.24, where it is supposed constant specific heat, \( c \) and \( v_m \) is the average specific volume between \( P \) and \( P_0 \):

\[ b_{\text{ph}} = c \left[ (T - T_0) - T_0 \ln \left( \frac{T}{T_0} \right) \right] + v_m(P - P_0) \]  

As indicated by Eqs. 2.22–2.24, the determination of the physical exergy requires only that the environment be defined by its ambient pressure and temperature, or reference pressure and temperature (\( P_0 \) and \( T_0 \)).

The concept of chemical exergy means the maximum work that it is possible to be performed when a given system (or mass flow rate) is taken from the restricted reference state up to the dead state in which there is a complete thermodynamic equilibrium: mechanical, thermal, and chemical equilibrium. In that evolution, the system is submitted to reversible processes interacting only with the environment. The chemical exergy of a system is given by:

\[ B_{\text{ch}}^s = U^* + P_0 V^* - T_0 S^* - \sum_{i=1}^{n} \mu_{0,i} N_i = \sum_{i=1}^{n} (\mu_i^* - \mu_{0,i})N_i \]
And the chemical exergy of a mass flow rate is:

$$\bar{b}_{ch} = \bar{h} - T_0 \bar{s} - \sum_{i=1}^{n} \mu_{0,i} x_i$$  \hspace{1cm} (2.26)$$

With the expressions of the physical and chemical exergies, the total system exergy is:

$$B^s = U + P_0 V - T_0 S - \sum_{i=1}^{n} \mu_{0,i} N_i$$  \hspace{1cm} (2.27)$$

And for a mass flow rate:

$$\bar{b} = \bar{h} - T_0 \bar{s} - \sum_{i=1}^{n} \mu_{0,i} x_i$$  \hspace{1cm} (2.28)$$

Figure 2.4 summarizes the procedure to determine the total exergy, by calculating the physical and chemical components:

### 2.2.3 Chemical Exergy Calculation

The chemical exergy determination requires a model of the standard environment, as proposed by Szargut et al. [19]. This model is composed of the following reference substances, given an environment at $T_0 = 298.15$ K and $P_0 = 101.325$ kPa:

- Gaseous components of the atmosphere ($O_2$, $N_2$, $CO_2$, $H_2O$, $D_2O$, Ar, He, Ne, Kr, Xe);
• Solid reference substances of the crust of the Earth;
• Ionic reference substances of the sea;
• Molecular reference substances, nonionizable of the sea.

As stated above, the reference environment is characterized by substances of the atmosphere, earth crust, and seas, as shown in Fig. 2.5.

The chemical exergy of reference gases that compose the standard atmosphere is given by the isothermal expansion work that could be performed in a turbine that exchanges heat with the environment at $T_0$ and takes the gas from $P_0$ up to its partial pressure in the standard atmosphere ($p_{00}$), as presented by Eq. 2.29:

$$
\bar{b}_{ch} = \bar{R}T_0 \ln \left( \frac{P_0}{P_{00}} \right) \quad (2.29)
$$

For a pure substance that does not exist in the reference environment, the chemical exergy is determined considering two reversible processes. The first one
is a reference chemical reaction that happens at $P_0$ and $T_0$ where the substance reacts with substances brought from the environment (coreactants) and generating substances that exist in the reference environment (products). The second process is a change in the concentrations of coreactants (from the state they are in equilibrium in the reference environment to the state they are pure at $P_0$ and $T_0$) and the concentration of the products (from $P_0$ and $T_0$ to the state they are in equilibrium in the reference environment) as shown in Fig. 2.6. The chemical exergy is then calculated as indicated in Eq. 2.30:

$$b_{\text{ch}} = -\Delta G_0 - \left[ \sum_i x_i \bar{b}_{\text{ch},i} \right] \text{coreactants} + \left[ \sum_j x_j \bar{b}_{\text{ch},j} \right] \text{products} \tag{2.30}$$

with,

$$\Delta G_0 = \sum_j v_j g_j - \sum_k v_k g_k \tag{2.31}$$

In Eq. 2.31, $v_k$, $v_j$, $g_k$ and $g_j$ are, respectively, the stoichiometric coefficients and the free Gibbs energy in molar basis. Index $j$ represents the products and index $k$ represents the reactants of the reaction (substance under study and coreactants).

For a mixture, the chemical exergy can be calculated as:

$$b_{\text{ch, mist}} = \sum_i x_i \bar{b}_{\text{ch},i} + R T_0 \sum_i x_i \ln \gamma_i x_i \tag{2.32}$$

where $x_i$ is the molar fraction of component “$i$”, $R$ is the universal gas constant, and $\gamma_i$ is the activity coefficient. For ideal mixtures, the activity coefficient is equal to one.

The chemical exergy of fuels can be evaluated as a function of the lower heating value (LHV), by means of expressions such as:

$$b_{\text{ch}} = \phi \text{LHV} \tag{2.33}$$

where $\phi$ can be determined by using correlations based on the composition of the fuel, as presented by Szargut et al. [19] and Kotas [8]. As examples, $\phi$ is about 1.04 for natural gas [8] and 1.08 for petroleum [17].

Example 2.1 Determine the chemical exergy of methane. The reference reaction for the determination of the chemical exergy of methane is the combustion reaction of methane with oxygen:

$$\text{CH}_4 + 2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{CO}_2$$

The determination of the chemical exergy of methane will be done by using two procedures. The first one determines the chemical exergy by solving Eqs. 2.30 and 2.31:

$$\bar{b}_{\text{ch,CH}_4} = -\Delta G_0 - 2b_{\text{ch, O}_2} + 2b_{\text{ch, H}_2\text{O}} + b_{\text{ch, CO}_2}$$
\[ \Delta G_0 = \text{Enthalpy (CH}_4; \ T = 25 \ ^\circ\mathrm{C}) + 2 \ \text{Enthalpy (O}_2; \ T = 25 \ ^\circ\mathrm{C}) \ - \ \text{Enthalpy (CO}_2; \ T = 25 \ ^\circ\mathrm{C}) \ - 2 \ \text{Enthalpy (H}_2\text{O}; \ T = 25 \ ^\circ\mathrm{C}) \ - 298.15 \ \text{[Entropy (CH}_4; \ T = 25 \ ^\circ\mathrm{C}; \ P = 101.325 \ \text{kPa}) + 2 \ \text{Entropy (O}_2; \ T = 25 \ ^\circ\mathrm{C}; \ P = 101.325 \ \text{kPa}) - 2 \ \text{Entropy (H}_2\text{O}; \ T = 25 \ ^\circ\mathrm{C}; \ P = 101.325 \ \text{kPa})]}\]

The values of enthalpies, entropies, and chemical exergies of the coreactants and products presented in the reference reaction and considered as ideal gases are shown in Table 2.2. This table also presents the entropy of the coreactants and products at the state they are in the reference environment, or dead state. In this table, the chemical exergy of these ideal gases is calculated according to Eq. 2.29:

These properties together with the enthalpy and entropy of methane at \(T_0\) and \(P_0\):

\[ h_{\text{CH}_4} = -74,595 \ \text{kJ/kmol} \]
\[ s_{\text{CH}_4} = 186.3 \ \text{kJ/kmol K} \]

allows the calculation of \(\bar{b}_{\text{chCH}_4}\):

\[ \bar{b}_{\text{chCH}_4} = 831, 862 \ \text{kJ/kmol CH}_4 \]

The second procedure to determine \(\bar{b}_{\text{chCH}_4}\), that requires only the values of enthalpies and entropies of the substances involved in the reference reaction, consists in applying energy and entropy balances to the control volume indicated in Fig. 2.7 in which there are reversible processes and the heat transfer interactions occur with the environment at \(T_0\). Methane (at \(P_0, T_0\)), and oxygen (at \(P_{00} \text{O}_2, T_0\)) enter the control volume, while water (at \(P_{00} \text{H}_2\text{O}, T_0\) and carbon dioxide (at \(P_{00} \text{CO}_2, T_0\)) leave it. The reversible work that can be obtained from the control volume is the chemical exergy of methane, given by:

\[ \bar{b}_{\text{chCH}_4} = \text{Enthalpy (CH}_4; \ T = 25 \ ^\circ\mathrm{C}) + 2 \ \text{Enthalpy (O}_2; \ T = 25 \ ^\circ\mathrm{C}) \ - \ \text{Enthalpy (CO}_2; \ T = 25 \ ^\circ\mathrm{C}) \ - 2 \ \text{Enthalpy (H}_2\text{O}; \ T = 25 \ ^\circ\mathrm{C}) \ - 298.15 \ \text{[Entropy (CH}_4; \ T = 25 \ ^\circ\mathrm{C}; \ P = 101.325 \ \text{kPa}) + 2 \ \text{Entropy (O}_2; \ T = 25 \ ^\circ\mathrm{C}; \ P = 20.43 \ \text{kPa})] \]
2.2 Exergy and Exergy Balance

- Entropy (CO₂; T = 25 °C; P = 0.03347 kPa) – 2 Entropy (H₂O; T = 25 °C; P = 2.2 kPa)]

\[ \bar{b}_{\text{CH}_4} = 831,874 \text{ kJ/kmol CH}_4 \]

The small difference between the values of \( \bar{b}_{\text{CH}_4} \) is due to some approximations made in the calculation of the thermodynamic properties.

Note that this second procedure for the determination of the chemical exergy of the methane is similar to calculation of the chemical exergy by using the following equation:

\[ \bar{b}_{\text{CH}_4} = h_{\text{CH}_4} - h_{\text{CH}_40} - T_0(s_{\text{CH}_4} - s_{\text{CH}_40}) \]

where:

- \( h_{\text{CH}_40} = \text{Enthalpy (CO}_2; T = 25 \circ C) + 2 \text{ Enthalpy (H}_2\text{O}; T = 25 \circ C) - 2 \text{ Enthalpy (O}_2; T = 25 \circ C) \)
- \( s_{\text{CH}_40} = \text{Entropy (CO}_2; T = 25 \circ C; P = 0.03347 \text{ kPa}) + 2 \text{ Entropy (H}_2\text{O}; T = 25 \circ C; P = 2.2 \text{ kPa}) - 2 \text{ Entropy (O}_2; T = 25 \circ C; P = 20.43 \text{ kPa}) \)

**Example 2.2** Methane is burnt with air. The mixture air methane enters the reactor at \( T_i = T_0 = 25 \circ C \) and \( P_i = 101.325 \text{ kPa} \). The combustion products leave the reactor, considered adiabatic, at \( P_e = 101.325 \text{ kPa} \) and at the adiabatic flame temperature \( (T_e) \). Determine the exergy destruction per kmol of methane, considering that reactants and products can be modeled as ideal gases and with percent excess air ranging from 0 up to 180 % (1 ≤ ε ≤ 2.8).

The combustion reaction of methane with air is given by:

\[ \text{CH}_4 + 2\varepsilon(\text{O}_2 + 3.762\text{N}_2) \rightarrow 2\text{H}_2\text{O} + \text{CO}_2 + 7.524\varepsilon\text{N}_2 + 2(\varepsilon - 1)\text{O}_2 \]

As the reactor is supposed to be adiabatic, the temperature of the combustion gases, the adiabatic flame temperature, \( T_e \), is determined by solving the reactor energy balance in which the enthalpy of the reactants is equal to the enthalpy of products:

\[ H_{\text{reactants}} = H_{\text{products}} \]
With:
\[ H_{\text{reactants}} = \text{Enthalpy (CH}_4; \ T = T_0) + 7.524 \times \text{Enthalpy (N}_2; \ T = T_0) + 2 \times \text{Enthalpy (O}_2; \ T = T_0) \]
\[ H_{\text{products}} = \text{Enthalpy (CO}_2; \ T = T_e) + 2 \times \text{Enthalpy (H}_2\text{O}; \ T = T_e) + 7.524 \times \text{Enthalpy (N}_2; \ T = T_e) + 2(\alpha - 1) \times \text{Enthalpy (O}_2; \ T = T_e) \]

The exergy of the reactants is done by:
\[ B_{\text{reactants}} = \bar{b}_{\text{ch CH}_4} + 2 \times \bar{b}_{\text{ch O}_2} + 7.524 \times \bar{b}_{\text{ch N}_2} + 298.15 \text{M} \bar{R} [1/\text{M ln}(1/\text{M}) + 7.524 \times \text{M ln}(7.524 \times \text{M}) + 2 \times \text{M ln}(2 \times \text{M})] \]

With:
\[ M = 1 + 9.524 \times (\text{number of mols of reactants}) \]
\[ \bar{R} = 8.314 \text{kJ/kmol K} \]

The exergy of the reactants can also be determined, as shown in Example 2.1, by:
\[ B_{\text{reactants}} = H_{\text{reactants}} - H_{\text{reactants0}} - 298.15 (S_{\text{reactants}} - S_{\text{reactants0}}) \]

In this equation, \(S_{\text{reactants}}\), \(H_{\text{reactants0}}\), and \(S_{\text{reactants0}}\) are, respectively, the entropy of reactants, enthalpy, and entropy of reference of the reactants at the dead state, given by:
\[ S_{\text{reactants}} = \text{Entropy (CH}_4; \ T = T_0; \ P = P_{\text{CH}_4}) + 7.524 \times \text{Entropy (N}_2; \ T = T_0; \ P = P_{\text{N}_2}) + 2 \times \text{Entropy (O}_2; \ T = T_0; \ P = P_{\text{O}_2}) \]
\[ H_{\text{reactants0}} = 2(\alpha - 1) \times \text{Enthalpy (O}_2; \ T = T_0) + \text{Enthalpy (CO}_2; \ T = T_0) + 2 \times \text{Enthalpy (H}_2\text{O}; \ T = T_0) + 7.524 \times \text{Enthalpy (N}_2; \ T = T_0) \]
\[ S_{\text{reactants0}} = 2(\alpha - 1) \times \text{Entropy (O}_2; \ T = T_0; \ P = P_{\text{00 O}_2}) + \text{Entropy (CO}_2; \ T = T_0; \ P = P_{\text{00 CO}_2}) + 2 \times \text{Entropy (H}_2\text{O}; \ T = T_0; \ P = P_{\text{00 H}_2\text{O}}) + 7.524 \times \text{Entropy (N}_2; \ T = T_0; \ P = P_{\text{00 N}_2}) \]

With:
\[ P_{\text{CH}_4} = P_i/\text{M} \]
\[ P_{\text{N}_2} = 7.524 \times P_i/\text{M} \]
\[ P_{\text{O}_2} = 2 \times P_i/\text{M} \]

Analogously, the exergy of products is given by:
\[ B_{\text{product}} = H_{\text{product}} - H_{\text{products0}} - 298.15 (S_{\text{product}} - S_{\text{products0}}) \]
With:

\[ H_{\text{products}} = \text{Enthalpy} (\text{CO}_2; T = T_e) + 2 \text{Enthalpy} (\text{H}_2\text{O}; T = T_e) + 7.524 \, z \text{Enthalpy} (\text{N}_2; T = T_e) + 2(z - 1) \text{Enthalpy} (\text{O}_2; T = T_e) \]

\[ S_{\text{products}} = \text{Entropy} (\text{CO}_2; T = T_e; P = P_{\text{CO}_2}) + 2 \text{Entropy} (\text{H}_2\text{O}; T = T_e; P = P_{\text{H}_2\text{O}}) + 7.524 \, z \text{Entropy} (\text{N}_2; T = T_e; P = P_{\text{N}_2}) + 2(z - 1) \text{Entropy} (\text{O}_2; T = T_e; P = P_{\text{O}_2}) \]

Where:

\[ P_{\text{CO}_2} = \frac{P_e}{M} \]
\[ P_{\text{H}_2\text{O}} = 2\frac{P_e}{M} \]
\[ P_{\text{N}_2} = 7.524 \, z \frac{P_e}{M} \]
\[ P_{\text{O}_2} = 2(z - 1) \frac{P_e}{M} \]

Taking into account the products of the combustion reaction:

\[ H_{\text{reactants}} = H_{\text{products}} \]
\[ S_{\text{reactants}} = S_{\text{products}} \]

As the reactor is adiabatic, \( H_{\text{reactants}} = H_{\text{products}} \), then:

\[ B_{\text{dest}} = B_{\text{reactants}} - B_{\text{products}} = 298.15 \, (S_{\text{products}} - S_{\text{reactants}}) = T_0S_{\text{ger}} \]

The relative exergy destroyed during the combustion reaction can be calculated as:

\[ \Delta_{\text{comb}} = \frac{B_{\text{dest}}}{B_{\text{reactants}}} \]

Table 2.3 presents the values of \( T_e \), \( B_{\text{reactants}} \), \( B_{\text{products}} \), \( B_{\text{dest}} \) and \( \Delta_{\text{comb}} \) for excess air ranging from 0 up to 180 % (1 \leq z \leq 2.8)
Figures 2.8 and 2.9 present the behavior of $T_e$ and $B_{\text{dest}}$ with the percent excess air, showing that the higher the percent excess air, the greater the exergy destroyed because the excess air mass dilutes the combustion gases, lowering the thermal exergy of the mixture of gases, and thus, reducing its capacity to perform work. This conclusion is particularly useful when studying gas turbines combustors, because the exergy destroyed in the combustor is a direct measure of the reduction
capacity of the turbine to generate mechanical or electrical power. This result also evidences that the quality of combustion is proportional to its adiabatic flame temperature [21].

2.3 Exergy: Graphical Representations and Exergy Diagrams

2.3.1 Introduction

The use of thermodynamic diagrams to represent processes, properties, as well as to determine work and heat quantities is a common practice in Engineering Thermodynamics. In the case of the Exergy Analysis of energy conversion processes, diagrams such as entropy–enthalpy and exergy–enthalpy are very useful to help the understanding and the evaluation of these processes.

In the next sections, the most important diagrams are presented for the determination of physical exergy, the exergy transferred and destroyed, the exergy of separation, and mixing of a binary mixture.

2.3.2 The Physical Exergy in the Enthalpy–Entropy Diagram

The physical exergy of a pure substance is easily determined in a Mollier diagram, as shown in Fig. 2.10. Giving the states represented by points $m\,(P,\,T)$ and $O\,(P_0\,\text{and}\,T_0)$ and drawing the line from point $O$ and with angle $\alpha$, $T_0$ can be determined by:

$$\left(\frac{dh}{ds}\right)_{P_0} = T_0 = \tan \alpha$$

This segment is called reference line and it is tangent to the isobaric that passes by $P_0$. Then it is possible to write Eq. 2.35:

$$\left(s_m - s_o\right) \tan \alpha = \left(s_m - s_o\right) T_0$$

And introducing the expression of the physical exergy, one gets:

$$b_{ph} = h_m - h_o - \left(s_m - s_o\right) \tan \alpha$$

2.3.3 Diagram Carnot Factor-Enthalpy

The first reference to the use of the diagram Carnot factor-enthalpy is attributed to Thring [21] for the study of combustion processes, where he introduced the concept of virtue of energy. This diagram is particularly useful for the study of heat transfer processes. In the abscissae axis it is represented the heat transfer rate
from one mass flow, determined by the variation of the enthalpy flow rate of this mass flow. The Carnot factor ($\theta = T_0/T$) is represented in the ordinate axis in order to characterise the temperature level in which the heat transfer takes place, as shown in Fig. 2.11 where it is represented the heat transfer process in a sugarcane juice heater of a sugar and alcohol mill. In this heat exchanger steam is used to heat the juice extracted from sugarcane.

By using the expression of the physical exergy (Eq. 2.22) and calculating the partial derivative, as indicating in Eq. 2.37, one can show that the Carnot factor indicates the change of the physical exergy with respect to enthalpy in a isobaric process.

$$\left(\frac{\partial b}{\partial h}\right)_p = 1 - \frac{T_0}{T} = \theta$$ (2.37)

It can be seen in this diagram that the area under the upper curve corresponds to the exergy transferred from the steam (heating agent) and the area under the lower curve is the exergy received by the sugarcane juice. The difference between these two values is the destroyed exergy rate in the heat transfer process.

This type of diagram was utilized by Le Goff et al. [9] for the study of the distillation of a binary mixture, as shown in Fig. 2.12. The corresponding diagram $\theta - \Delta H$ is presented in Fig. 2.13.
Considering that in the reboiler the heating agent passes from temperature $T_{b1}$ to $T_{b2}$, in order to vaporize the liquid at $T_B$, and the condenser is cooled by a fluid in which temperature increases from $T_{c1}$ to $T_{c2}$, to condensate the vapor at $T_D$, it is possible to represent in the diagram $\theta - \Delta H$ the heat rate quantities $Q_B$ e $Q_C$ (see Fig. 2.13). The area between the line at $\theta_B$ and the line at $\theta_D$ is the net thermal exergy rate supplied to the separation process ($B_t$) and it is composed of the

Fig. 2.11 Diagram Carnot factor ($\theta$)--$\Delta H$ for a heating juice system of a sugar and alcohol mill [14]

Fig. 2.12 Typical scheme of a binary distillation set [9]
separation exergy \( (B_{\text{sep}}) \) and the destroyed exergy \( (B_{\text{dest}}) \) as shown by Eqs. 2.38 and 2.39.

\[
B_t = Q_B \theta_B - Q_C \theta_D \tag{2.38}
\]

\[
B_t = B_{\text{dest}} + B_{\text{sep}} \tag{2.39}
\]

The main limitation to the use of this diagram is that it is not possible to represent the exergy destroyed due to the head loss in the heat exchanger.

### 2.3.4 Diagram Exergy–Enthalpy

The diagram exergy–enthalpy gives all necessary information to analyze a given energy conversion process of a pure substance, for the application of energy and exergy balances. Figure 2.14 presents a typical exergy–enthalpy diagram. As pointed out in Sect. 2.3.3, based on the physical exergy definition, one can obtain the following expression:

\[
(\partial b/\partial h)_s = 1 \tag{2.40}
\]

That is, in this diagram, the isentropic lines are inclined at 45° with respect to the enthalpy axis when both variables are represented with the same scale.
2.3.5 Diagrams Exergy-Composition and Exergy–Enthalpy for Binary Mixtures

The diagram exergy-composition for binary mixtures is analogous to the enthalpy-concentration diagram, being particularly useful in the study and optimization of absorption refrigerating and heat pump systems that work with mixtures H$_2$O—LiBr and NH$_3$—H$_2$O. Oliveira [13] proposed a simple procedure to calculate the exergy of a solution and to build these diagrams based on the definition of equilibrium solutions at $P_0$, $T_0$, the reference environment pressure and temperature. This procedure is adequate for systems that operate in closed circuit, such as absorption heat pumps and refrigerating systems, avoiding the necessity to use the reference conditions proposed by Szargut et al. [19].

First it is considered the calculation of the exergy of a binary mixture in which its components exist pure at $P_0$, $T_0$. Then it is considered a process where the studied mixture changes its thermodynamic state from state $M (T_M, P_M, X_M)$ up to a state where $P = P_0$ and $T = T_0$, maintaining the same concentration. Then the mixture is completely separated in a isothermal process ($x = 0$ and $x = 1$). Finally, every component will change its pressure up to $P_0$, as shown in Fig. 2.15. This sequence of processes can be associated with those that take place in a separation process presented in Fig. 2.16. The separation exergy of the mixture $M$ is in fact the exergy of the state $M$, given by Eq. 2.41:

$$b_m = [h_M - (1 - x_M)h_{A0} + x_Mh_{B0}] - T_0[s_M - (1 - x_M)s_{A0} + x_Ms_{B0}]$$ (2.41)

In this case, the reference enthalpy and entropy of the mixture $M$ are given by Eqs. 2.42 and 2.43:
\[ h_{M0} = (1 - x_M)h_{A0} + x_Mh_{B0} \]  
(2.42)

\[ s_{M0} = (1 - x_M)s_{A0} + x_Ms_{B0} \]  
(2.43)
and in the particular case of the exergy determination of pure substances \((x_M = 0\) or \(x_M = 1\)), one has:

\[ h_{M0} = h_{A0} \quad \text{or} \quad h_{M0} = h_{B0} \]

\[ s_{M0} = s_{A0} \quad \text{or} \quad s_{M0} = s_{B0} \]

When there is a mixture at \(T_0\) and \(P_0\), as is the case for mixtures NH\(_3\)—H\(_2\)O, at the exit of the separator there will be a mixture at \(x_0\) and one pure substance \((x = 0\) or \(x = 1\)), as indicated in Fig. 2.16. Now there are two possible reference conditions:

- \(T_0, P_0, x_0\) and \(T_0, P_0, x = 0\)
- \(T_0, P_0, x_0\) and \(T_0, P_0, x = 1\)

For the first case, the reference enthalpy and entropy are given by Eqs. 2.44 and 2.45:

\[
h_{M0} = \left(\frac{x_m}{x_0}\right)h_0 + \left(1 - \frac{x_m}{x_0}\right)h_{A0} \tag{2.44}
\]

\[
s_{M0} = \left(\frac{x_m}{x_0}\right)s_0 + \left(1 - \frac{x_m}{x_0}\right)s_{A0} \tag{2.45}
\]

For the second case, one has:

\[
h_{M0} = \left(\frac{1 - x_m}{1 - x_0}\right)h_0 - \left(\frac{x_0 - x_m}{1 - x_0}\right)h_{A0} \tag{2.46}
\]

\[
s_{M0} = \left(\frac{1 - x_m}{1 - x_0}\right)s_0 - \left(\frac{x_0 - x_m}{1 - x_0}\right)s_{A0} \tag{2.47}
\]

The described procedure was utilised in the development of diagrams exergy—enthalpy of binary mixtures H\(_2\)O—LiBr and NH\(_3\)—H\(_2\)O shown in Figs. 2.17 and 2.18. In these diagrams, the partial derivative \((\partial b/\partial h)_p\) gives:

\[
(\partial b/\partial h)_p = 1 - T_0(\partial s/\partial h)_p \tag{2.48}
\]

This term can be considered a modified Carnot factor for a mixture/solution, and the analysis of its behavior is useful in the determination of the optimal operating conditions of a separator or a mixer [13].

### 2.3.6 Grassmann Diagram

The Grassmann diagram [7] is a graphical representation similar to the well-known Sankey diagram employed in the energy analysis of processes, where the width of the bands is associated to the exergy rate or exergy flow rate of a given energy.
conversion process. Considering a cogeneration plant shown in Fig. 2.19, the Sankey and Grassmann diagrams are presented, respectively, in Figs. 2.20 and 2.21.

It is interesting to notice that in both diagrams the difference of the values of energy and exergy bands. The Grassmann diagram evidences that the component of the plant that is the main responsible for the exergy destruction in the processes is the boiler, because of the highly irreversible processes that take place inside it: the combustion reaction and the heat transfer between the combustion products and the water. It is due to this exergy destruction that the overall efficiency conversion: fuel chemical exergy into mechanical/electrical work is about 30 % in conventional thermal power plants that operates based on Rankine cycles.

2.4 Exergy Efficiency

2.4.1 Balance of the Energy Value

Given an energy conversion system, shown in Fig. 2.22, that receives an energy rate amount $E_i$, supplies a useful energy rate $E_u$, and rejects $E_w$, the energy balance is done by Eq. 2.49:

$$E_i = E_p + E_w$$  \hspace{1cm} (2.49)
As emphasized by Le Goff et al. [9], an economist would see this process in a different way. It consists of a system that converts goods of small value into goods with added value by means of consuming expensive goods (such as raw materials, energy, information, capital, etc.) and generating wastes with reduced value that are rejected into the environment, as represented in Fig. 2.22 in the production and utilization phases.

The balance of value of this process can be written as:

\[ E_i v_i + C_o = E_p v_p + E_w v_w \]  \hspace{1cm} (2.50)

In this expression the terms \( v \) are the ‘values’ that are given to every energy rate or flow rate and \( C_o \) is the operational energy cost rate (see Eq. 2.51)

Combining Eqs. 2.49 and 2.50 one obtains the expression of the operational cost rate:

---

**Fig. 2.18** Diagram exergy–enthalpy for water–lithium–bromide solutions \((T_0 = 25 \degree C, \ P_0 = 1\text{bar}, \ x_{0A} = 0 \text{ and } x_0 = 20 \%)\) [13]

**Fig. 2.19** Simplified cogeneration plant

As emphasized by Le Goff et al. [9], an economist would see this process in a different way. It consists of a system that converts goods of small value into goods with added value by means of consuming expensive goods (such as raw materials, energy, information, capital, etc.) and generating wastes with reduced value that are rejected into the environment, as represented in Fig. 2.22 in the production and utilization phases.

The balance of value of this process can be written as:

\[ E_i v_i + C_o = E_p v_p + E_w v_w \]  \hspace{1cm} (2.50)

In this expression the terms \( v \) are the ‘values’ that are given to every energy rate or flow rate and \( C_o \) is the operational energy cost rate (see Eq. 2.51)

Combining Eqs. 2.49 and 2.50 one obtains the expression of the operational cost rate:
Dividing Eq. 2.51 by $E_u$, one obtains the specific operational cost:

$$C_o = \frac{C_o}{E_u} = E_p (v_p - v_i) + \frac{E_W}{E_u} (v_w - v_i) \quad (2.51)$$

The first term in the right side of Eq. 2.52 is the value gain of the products and the second term is the loss of value of the wastes.

2.4.2 General Definition of Efficiency

The performance of a given process or equipment can be defined by the following expression of efficiency:
For an energy system whose objective is to perform a given energy conversion, its efficiency can be given as:

\[
\eta = \frac{\sum (\text{value of products})}{\sum (\text{value of inputs})}
\]

Fig. 2.22 Energy and value balance

\[
\eta = \frac{\sum (E_u v_u)}{\sum (E_i v_i)}
\]

It is important to note that this definition does not imply, necessarily, that \( \eta \) < 1 as will be further discussed.

According to the utilized energy value scale, Eq. 2.54 can provide different information.

The first scale postulates that every energy form has the same value.

\[
v_a = v_u = v_w = v_i = v_f
\]

In this case, the value balance is equal to the energy balance, or the First Law of Thermodynamics, and the efficiency expression is the energy efficiency. The energy efficiency of thermal engines is the thermal efficiency, which is always lower than one, and the energy efficiency of heat pumps and refrigerating systems is the coefficient of performance, that can be higher or lower than one.

A second value scale consists in associating to a given energy quantity its corresponding value of exergy, for instance:

– For work:

\[
v_w = 1
\]

– For heat:

\[
v_Q = \left( 1 - \frac{T_0}{T} \right)
\]
– For an enthalpy change of a pure substance:

\[ v_H = 1 - T_0 \left( \frac{s_1 - s_2}{h_1 - h_2} \right) \] 

With this value scale, the efficiency expression becomes the exergy efficiency and its value will be always lower than one (it will be one for an internally and externally reversible process).

It is interesting to note that when the energy value scale is used, the specific operational cost will be zero, as a consequence of the First Law of Thermodynamics. Also, when the exergy value scale is employed for a heat engine, its specific operational cost will be zero for a Carnot engine and will be negative, for a real heat engine, due to the occurrence of irreversible processes (the output exergy is lower than the input exergy).

### 2.4.3 Exergy Efficiency

In the exergy literature there are many expressions to quantify the exergy performance of energy conversion processes ([16, 19, 22]). Three definitions will be presented next. They are commonly applied to analyze the performance of chemical processes, thermal engines, and dissipative processes.

The first expression (Eq. 2.59), called degree of perfection by Szargut et al. [19] is useful to evaluate chemical processes:

\[ \eta_p = \frac{\text{Exergy of useful products}}{\text{Feeding exergy}} \] 

The second expression is similar to Eq. 2.59 and is indicated in the analysis of thermal processes:

\[ \eta_{b1} = \frac{\text{Useful exergy effect}}{\text{Driving exergy}} \] 

For thermal engines and refrigerating system that interact with the environment, Eq. 2.60 can be rewritten as:

\[ \eta_{b2} = \frac{\eta_c}{\eta_{\text{carnot}}} = \frac{\eta_e}{\eta_{\text{e max}}} \] 

The third expression is recommended to be used to quantify the performance of processes and equipment where the only effect is the exergy destruction, such as the flow of steam through an expansion valve, or the heat rejection that takes place in a condenser of a thermal power plant, or in the condenser of a refrigerating system. These processes are usually called pure dissipative processes.
In order to apply the concept of the exergy efficiency, consider the determination of the exergy efficiency of a two stage heat transformer that has to heat up a particular mass flow rate from 100 to 120 °C, by using a thermal waste available at 85 °C. This heat transformer operates according to an absorption cycle with water-lithium bromide as the working pair, as represented in Fig. 2.23.

The mixer (absorber–evaporator set) is composed of two evaporation/absorption sets in thermal series and in a parallel arrangement for the solution and water flow rates that enters the mixer (see Fig. 2.23). The aqueous solutions of lithium bromide enter and leave the absorbers with salt concentrations of, respectively, 60 and 50 %. The water saturation pressures in both effects are 35.3 and 97.6 kPa,
respectively. The separator (generator–condenser set) operates under a pressure of 5.3 kPa.

The processes that take place in the mixer and in the separator are represented in a diagram exergy–enthalpy, shown in Fig. 2.24 ($T_0 = 25 \degree C$, $P_0 = 1\text{bar}$, $x_{OA} = 0$ and $x_0 = 20 \%$). Based on the data of states indicated in Fig. 2.25, it is possible to develop the energy and exergy balances for every component of the heat transformer, and calculate the parameters presented in Table 2.4. Considering additionally the inlet and outlet temperatures of the mass flow rates indicated in Fig. 2.24, a minimum temperature difference of 3 $\degree C$ in the heat and mass exchangers and the required power ($W_p$) in the solution and water pumps, one can determine the exergy efficiencies of the separator ($\eta_{sep}$), mixer ($\eta_{mix}$), and the heat transformer ($\eta_{htr}$).

Fig. 2.24  Heat transformer processes representation in the water lithium bromide exergy–enthalpy diagram [13]

Fig. 2.25  Exergy balance of energy conversion processes
Table 2.4 Results of the energy and exergy balances

<table>
<thead>
<tr>
<th>Energy balances (kJ/kg water)</th>
<th>Exergy balances (kJ/kg water)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Q_{cd} = 5069 )</td>
<td>( \Delta b_{cd} = 112.8 )</td>
</tr>
<tr>
<td>( Q_{de} = 5809 )</td>
<td>( \Delta b_{sep} = 627.6 )</td>
</tr>
<tr>
<td>( Q_{ev1} = 2329 )</td>
<td>( \Delta b_{ev1} = 317.9 )</td>
</tr>
<tr>
<td>( Q_{ev2} = 2471 )</td>
<td>( \Delta b_{ev2} = 436.0 )</td>
</tr>
<tr>
<td>( Q_{ab} = 2628 )</td>
<td>( \Delta b_{mix} = 607.9 ) (for both stages)</td>
</tr>
</tbody>
</table>

\[
\eta_{sep} = \frac{\Delta b_{sep}}{Q_{dc} \theta_{dc} - Q_{cd} \theta_{cd}} = 0.504
\]

\[
\eta_{mix} = \frac{Q_{ab} \theta_{ab} - Q_{ev} \theta_{ev}}{\Delta b_{mix}} = 0.353
\]

\[
\eta_{btt} = \frac{Q_{ab} \theta_{ab}}{W_p + Q_{dc} \theta_{dc} + Q_{ev} \theta_{ev}} = 0.462
\]

The obtained results allow determining the exergy performance of the proposed heat transformer, as well as the performance of its components. With this information it is possible to identify which are the most important components in the overall performance of the system.

### 2.4.4 Environmental Exergy Efficiency (\( \eta_{b,env} \))

The environmental impact of the energy conversion processes can be reduced by the increase of the exergy efficiency of these processes. An increase in the exergy efficiency would have as a consequence, a decrease in the consumption of resources and thus a reduction of the wastes and the emissions to the environment. This implies an improvement in the environmental performance of these processes.

The environmental exergy efficiency is defined as the ratio of the final product exergy (or useful effect of a process) to the total exergy of natural and human resources consumed, including all the exergy inputs in a given energy conversion process. This ratio is also an indication of the theoretical potential of future improvements for a process. The environmental exergy efficiency is calculated in agreement with Eq. 2.63:

\[
\eta_{b,env} = \frac{B_{product}}{B_{nat, res} + B_{processing} + B_{utilities} + B_{deactivation} + B_{disposal}} \quad (2.63)
\]

where:
- \( B_{product} \) exergy rate of the useful effect of a process
- \( B_{nat, res} \) exergy rate of the natural resources consumed by the processes
- \( B_{processing} \) exergy rate or flow rate required for extraction and preparation of the natural resources
Figure 2.25 illustrates the Grassmann diagram of a given energy conversion process including the terms of Eq. 2.63 and the exergy flow rate of the reject sent to the environment $B_{\text{reject}}$.

The differences found in the literature, between the conventional definitions of the exergy efficiency and the environmental exergy efficiency, are based on the choice of different control volumes for each one of them. This fact determines the inclusion or exclusion of some terms of the total exergy consumed by human and natural resources, with the consequence that the values of the indexes are influenced by the definition of the boundaries of the considered system.

Mora and Oliveira [12] tried to encompass the exergy and environmental evaluation of iron making processes by using the environmental exergy efficiency. This study was based on data presented by Yagi and Akiyama [27]. They applied the exergy analysis to a conventional blast furnace iron making process without and with injection of 110 kg of pulverized coal, and examined the effect of high pulverized coal injection on the total exergy loss and on the emission of greenhouse effect gases. They demonstrated that the total exergy loss decreased when an amount of coke was replaced equally by pulverized coal, improving combustion with oxygen enrichment. With respect to the emission of the greenhouse effect gases, it was found that the injection of pulverized coal decreased by 5% the total emission of these gases, or 132 kg-C/thm (ton of hot metal). All greenhouse effect gases emitted (CO, CO$_2$, CH$_4$, etc.) were determined and converted into equivalent mass of CO$_2$, for the process without injection of pulverized coal, on the basis of the carbon mass (kg-C). They presented the data of the input, destroyed and lost exergy in GJ/thm (ton of hot metal) for both cases.

The exergy output for both processes was calculated by applying the exergy balance for these two processes. These data together with those obtained from the work of Yagi and Akiyama [27], the destroyed and lost (consumed) exergy and the emission of CO$_2$, are presented in Fig. 2.26.
To calculate the emission of CO$_2$ of the conventional blast furnace ironmaking process with injection of 110 kg of pulverized coal, it was taken as the reference the data of the decreasing rate of emission of 5% for 132 kg-C/thm of high pulverized coal injection presented by Yagi and Akiyama [27]. In this case, with 110 kg-C/thm of injected coal, it was obtained a decreasing emission of 4.16%, given a CO$_2$ emission value of 479.2 kg-C/thm. These results are shown in Fig. 2.27.

Observing the results of Figs. 2.26 and 2.27, it can be concluded that the process that causes the smallest impact in the environment is the conventional blast furnace ironmaking process with injection of 110 kg pulverized coal, due to the fact that it has the smallest destroyed and lost exergy (8.0 GJ/thm), and the smallest emission of CO$_2$ (479.2 kg-C/thm). These conclusions are coincident with that based on the values of the environmental exergy efficiency, as summarized in Table 2.5.

In this comparison, the values of the environmental exergy efficiency quantifies properly the quality of environmental solutions (pulverized coal injection) that aim at the decreasing the emissions of the greenhouse effect gases in the conventional blast furnace ironmaking process.

---

**Table 2.5** Values of the environmental exergy efficiency, destroyed and lost exergy, and CO$_2$ emissions for two ironmaking processes

<table>
<thead>
<tr>
<th>Process</th>
<th>$\eta_{b,env}$</th>
<th>Destroyed and lost exergy (GJ/thm)</th>
<th>CO$_2$ (kg-C/thm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional blast furnace ironmaking without pulverized coal injection</td>
<td>0.42</td>
<td>9.3</td>
<td>500.0</td>
</tr>
<tr>
<td>Conventional blast furnace ironmaking with injection of 110 kg pulverized coal</td>
<td>0.50</td>
<td>8.0</td>
<td>479.2</td>
</tr>
</tbody>
</table>

---

**Fig. 2.27** Exergy balance and CO$_2$ emission of the conventional blast furnace ironmaking with injection of 110 kg pulverized coal (thm = ton of hot metal) [12]
2.5 Exergy Costing

2.5.1 Introduction

The production cost determination in a multi-product energy conversion plant has several methodological challenges. Different approaches, based on the use of the concept of exergy have been proposed [4, 5, 8, 22, 24] regarding the cost partition methods in order to reduce the arbitrariness usually presented in the procedures that characterize the cost formation process of the products of a given plant.

Exergy-based cost analysis aims at determining the costs of products and irreversibilities (exergy destroyed) generated in energy conversion processes, by applying cost partition criteria which are function of the exergy content of every energy flow that takes place in the studied process. In this approach one studies the cost formation processes by valuing the products according to its exergy content and the destroyed exergy during the energy conversion processes. This combination of exergy analysis with economic concepts is called thermoeconomic analysis when monetary costs are used and exergoeconomic analysis when exergy costs are employed.

From the point of view of the modeling, simulation and optimization procedures of energy systems, the thermoeconomic or the exergoeconomic analysis aggregates, basically, two sets of equations: the cost balances (in fact, cost rate balances) for components/equipment or processes and the exergy-based cost partition criteria. As already mentioned by Tsatsaronis [22], the steps of thermoeconomic analysis comprise:

- detailed exergy and economic analysis of the components and the overall energy system;
- exergy costing;
- exergoeconomic evaluation of every component; and of the overall system.

It is important to emphasize that the more detailed the cost balances are, the better the results provided by the thermoeconomic or the exergoeconomic analysis will be.

The information generated by the thermoeconomic analysis are quite unlike from those provided by the traditional methods used for assessing the economic viability of energy-saving projects, such as those that determine, the net present value (NPV), the internal rate of return (IRR), and the payback period [3]. The thermoeconomic analysis allows the determination of production costs based on the quality of the energy conversion processes by using a rational criterion of costs distribution along the processes that is the thermodynamic value of each product, or its exergy [5, 22].

2.5.2 Cost Balance

The cost balance for a given component or equipment, operating in steady state, is done by Eq. 2.64:
Rate of expenses \( \Delta t \) = Rate of the products \( \Delta t \) \( \times \) Cost rate of the products \( \Delta t \) \( \times \) 2.64

The expenses are due to capital costs, operational, and maintenance costs.

For the control volume that embodies equipment and processes, shown in Fig. 2.28, with inputs a, b, and c (such as fuel, electricity, water, air, etc.) and products e, f, and g (such as steam, chilled water, electricity, mechanical power, etc.), the cost balance is done by Eq. 2.65.

\[ C_a + C_b + C_c + C_{\text{equipment}} = C_e + C_f + C_g \quad (2.65) \]

Every term of Eq. 2.65 has dimension of cost per unit of time ($/s), in a similar form used for mass, energy, and exergy balances in steady state conditions.

The average unitary cost, \( c_i \), is defined by Eq. 2.66 as:

\[ c_i = C_i / N_i \quad (2.66) \]

In Eq. 2.66, \( N_i \) can be a quantity such as mass flow rate, volumetric flow rate, energy rate/energy flow rate, exergy rate/exergy flow rate. Considering the control volume shown in Fig. 2.28, one can rewrite Eq. 2.65 as:

\[ c_a N_a + c_b N_b + c_c N_c + C_{\text{equipment}} = c_e N_e + c_f N_f + c_g N_g \quad (2.67) \]

When there are more than one product, as shown in Fig. 2.28, the values of \( c_e \), \( c_f \), and \( c_g \) cannot be determined only by the cost balance equation, being necessary additional equations based on a cost partition criterion such as:

- the products are for exclusive use of the analyzed plant;
- the products will be sold in the market;
- one product is considered a ‘primary product’ of the process;
- one product is considered to be a ‘by-product’ of the process, etc.

In the case there is only one product in the process, the cost balance determines the value of the average unitary cost:
2.5.3 Exergy-Based Cost Partition Criteria

When applying a thermoeconomic analysis one intends to use exergy-based cost partition criteria for the determination of the production costs in a multi-products equipment, components, or processes. A simple and effective approach to this problem consists in utilizing the equality method or the extraction method.

These two methods will be described by taking a cogeneration plant operating with a backpressure steam turbine, as shown in Fig. 2.29. In this plant there are two products: electricity and low pressure steam for heating purposes.

The cost balances for the steam generator and the steam turbine are given, respectively, by Eqs. 2.69 and 2.70.

\[ c_i = \frac{\text{Overall production cost}}{N_i \text{ product units}} \] (2.68)

\[ c_{hp} B_{hp} + c_{ef} B_{ef} + c_q B_q = c_{fuel} B_{fuel} + c_{air} B_{air} + c_{water} B_{water} + C_{sg} \] (2.69)

\[ c_e W_e + c_{lp} B_{lp} = c_{hp} B_{hp} + C_t \] (2.70)

In Eqs. 2.69 and 2.70, the exergy rates \( (B_q \text{ and } W_e) \) and exergy flow rates \( (B_{hp}, B_{ef}, B_{fuel}, B_{air}, B_{water}, B_{lp}) \) have been previously determined by the application of the energy and exergy balances to the steam generator and turbine.

The terms \( C_{sg} \) and \( C_t \) are, respectively, the cost rates of the steam generator and steam turbine, including capital, operational and maintenance costs of these components, obtained by an economic analysis. The costs of the inputs, fuel, water, and air, are considered known in the forthcoming analysis.
For the sake of simplicity, it will be taken into account that $B_q$ and $B_{ef}$ are wastes, or they are not products of the cogeneration plant. Then:

$$c_{ef} = c_q = 0$$ (2.71)

The determination of the exergy costs of the high pressure steam ($c_{hp}$), low pressure steam ($c_{lp}$), and electricity ($c_e$) requires three independent equations. As there are only two cost balances, one for each component, the third equation will be provided by a cost partition criterion.

**Equality method**

In this method the analyzed equipment/component must supply all exergy demands and consequently all products have the same exergy average cost. Then all the costs are divided among the products as a function of their exergy content. In the case of the steam turbine of Fig. 2.29, both products, electricity, and low pressure steam, must supply the exergy needs of the plant. In this way, the steam turbine capital, operational, and maintenance costs are shared to the two products, giving the additional equation:

$$c_e = c_{lp}$$ (2.72)

And the average cost of the products is:

$$c_e = c_{lp} = c_{hp} \left( \frac{B_{hp}}{B_{lp} + W_e} \right) + \frac{C_t}{(B_{lp} + W_e)}$$ (2.73)

In this case, one can define an exergy efficiency of the steam turbine as given by Eq. 2.74:

$$\eta_{\text{turbine}} = \frac{W_e + B_{lp}}{B_{hp}}$$ (2.74)

**Extraction method**

In this method, the studied equipment or component has only one function and the product of this function is charged with its capital, operational, and maintenance costs. In this way, the user of this product will pay the exergy rate spent as well as the capital, maintenance, and other operational costs. Then, the product of the steam turbine of the cogeneration plant is electricity, and the exergy cost of the low pressure steam is not affected by the existence of the turbine. This consideration provides the additional equation:

$$c_{hp} = c_{lp}$$ (2.75)

It must be emphasized that although having the same exergy costs, the high pressure, and low pressure steam have different mass-based costs, because:

$$(c_{hp})_m = c_{hp}b_{hp}$$ (2.76)
and,

\[(c_{lp})_m = c_{lp} b_{lp}\]  \hspace{1cm} (2.77)

Then,

\[(c_{hp})_m > (c_{lp})_m\]

This result characterizes the higher thermodynamic value of the high pressure steam, and consequently, its higher mass-based cost.

In the case, the studied steam turbine is a condensation-extraction one, this criterion would give:

\[c_{lp} = c_{cd}\]  \hspace{1cm} (2.78)

and, as shown previously:

\[(c_{lp})_m > (c_{cd})_m\]

Taking Eq. 2.75 in the cost balance of the steam turbine, it is determined as the electricity cost:

\[c_e = c_{hp} \left( \frac{B_{hp} - B_{lp}}{W_e} \right) + \frac{C_t}{W_e}\]  \hspace{1cm} (2.79)

It is worthy of note that when applying the extraction method, the only product of the steam turbine is electricity (or mechanical work) and then its exergy efficiency is now defined as:

\[\eta_{\text{b turbine}} = \frac{W_e}{B_{hp} - B_{lp}}\]  \hspace{1cm} (2.80)

### 2.5.4 Application of the Thermoeconomic Analysis

The presented study describes how an exergy and thermoeconomic analysis can be applied to a cogeneration plant in order to determine the production cost of steam and electricity. Figure 2.30 represents this plant that supplies electricity and steam to an industrial process as described by Pellegrini et al. [15]

The plant operational data are the following:

- Steam generation (section 1): 490 °C at 100 bar;
- Percent excess air in the boiler: 100 %
- Methane flow rate: 1 kg/s;
- Methane cost: US$ 10.00/MWh (US$ 144.00/t)
- Methane lower heating value: 50,146 kJ/kg;
- Stack gases temperature: 240 °C;
• Air temperature: 25 °C;
• Water temperature at the condenser inlet: 25 °C;
• Water temperature at the condenser outlet: 45 °C;
• Extraction mass ratio: \( \frac{m_2}{m_1} = 0.5 \);
• Steam state at turbine section 5: 240 °C@2 bar;
• Condensation pressure: 0.07 bar;
• Quality at turbine section 2: 0.97;
• Pumps Isentropic efficiency: 80 %.
• Environment conditions: 25 °C and 1 bar

Based on these operational data and Eqs. 2.81 and 2.82, applied to each component of the plant and to the overall plant, it is possible to determine the thermodynamic properties of water (the working fluid) at every section indicated in Fig. 2.30, as shown in Table 2.6:

**Mass balance:**

\[
\sum_{\text{inlet}} m_i = \sum_{\text{outlet}} m_e \tag{2.81}
\]

**Energy balance:**

\[
\sum_{\text{inlet}} m_i h_i + Q_{VC} = W_{VC} + \sum_{\text{outlet}} m_e h_e \tag{2.82}
\]
Then Eqs. 2.83–2.85 can be solved to determine the energy and exergy performance of the plant.

**Exergy balance:**

\[
\sum_{\text{inlet}} m_i b_i + Q_{VC} \left(1 - \frac{T_0}{T}\right) = W_{VC} + \sum_{\text{inlet}} m_e b_e + I_{VC}
\]  

(2.83)

**Energy efficiency:**

\[
\eta_e = \frac{W_{\text{net}} + Q_{\text{process}}}{m_{\text{CH}_4}\text{LHV}}
\]  

(2.84)

**Exergy efficiency:**

\[
\eta_b = \frac{W_{\text{net}} + B_{\text{process}}}{m_{\text{CH}_4} b_{\text{CH}_4}}
\]  

(2.85)

Table 2.7 presents the performance parameters of the cogeneration plant.

The components capital cost can be estimated by using, for every component, the so-called exponential form as described by Bohem [2] and presented by the cost curve given in Eq. 2.86, where \( C_r \) is the cost of reference size component, \( C_{eq} \) is the cost of a size of interest, \( x \) is the exponent on cost size relationship, \( S_r \) is the component reference size, and \( S \) is the component size of interest (see Table 2.8).

\[
C_{eq} = C_r \left(\frac{S}{S_r}\right)^x
\]  

(2.86)

The following hypotheses are considered in the determination of the components cost rates:

– Capital recovery period (N): 20 years;
– Interest rate (i): 15 \% per year;
– Annual operating hours: 8000;
– Annual operational and maintenance factor (\( f_{O&M} \)): 1.06

<table>
<thead>
<tr>
<th>Section</th>
<th>Mass flow rate (kg/s)</th>
<th>Pressure (bar)</th>
<th>Temperature (K)</th>
<th>Specific enthalpy (kJ/kg)</th>
<th>Specific entropy (kJ/kg K)</th>
<th>Specific exergy (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.94</td>
<td>100.00</td>
<td>763.20</td>
<td>3348.00</td>
<td>6.56</td>
<td>1396.00</td>
</tr>
<tr>
<td>2</td>
<td>6.97</td>
<td>0.07</td>
<td>312.20</td>
<td>2499.00</td>
<td>8.04</td>
<td>106.10</td>
</tr>
<tr>
<td>3</td>
<td>6.97</td>
<td>0.07</td>
<td>312.20</td>
<td>163.40</td>
<td>0.56</td>
<td>1.24</td>
</tr>
<tr>
<td>4</td>
<td>6.97</td>
<td>100.00</td>
<td>313.00</td>
<td>175.90</td>
<td>0.57</td>
<td>11.41</td>
</tr>
<tr>
<td>5</td>
<td>6.97</td>
<td>2.00</td>
<td>513.20</td>
<td>2950.00</td>
<td>7.67</td>
<td>668.50</td>
</tr>
<tr>
<td>6</td>
<td>6.97</td>
<td>2.00</td>
<td>393.40</td>
<td>504.70</td>
<td>1.53</td>
<td>53.06</td>
</tr>
<tr>
<td>7</td>
<td>6.97</td>
<td>100.00</td>
<td>394.80</td>
<td>517.70</td>
<td>1.54</td>
<td>64.06</td>
</tr>
<tr>
<td>8</td>
<td>13.94</td>
<td>100.00</td>
<td>354.10</td>
<td>346.80</td>
<td>1.08</td>
<td>29.36</td>
</tr>
</tbody>
</table>

Table 2.6 Cogeneration plant data [15]
With these parameters the cost rates are obtained by Eq. 2.87 and 2.88 and the components values are presented in Table 2.9:

\[ C = \frac{C_{eq} f_a f_{O&I}}{3600 \times 8000} \]  
\[ f_a = \frac{i}{1 - (1 + i)^N} \]

With this information the cost balances can now be written for every component:

\[ \sum_{inlet} c_i B_i + C = \sum_{outlet} c_e B_e \]

In the cost balance equation of the steam turbine there are three unknowns: \( c_2 \), \( c_3 \), and \( c_e \), being necessary two additional equations to establish the relationships among \( c_1 \) and the three unknown variables. In this study both criteria described before will be used: the equality and the extraction methods, aiming at showing the differences they cause in the exergy-based cost values distribution.
The equality method gives the following equations:

\[ c_2 = c_e \]  
\[ (2.90) \]

\[ c_2 = c_5 \]  
\[ (2.91) \]

The extraction method considers that the product of the turbine is the electricity, then:

\[ c_1 = c_2 \]  
\[ (2.92) \]

and also:

\[ c_1 = c_5 \]  
\[ (2.93) \]

The process cost balance also requires a relationship between \( c_5 \) and \( c_6 \), because it is considered in the analysis as a black box (there is not available information about the use of the thermal exergy of the condensing steam when it changes its thermodynamic state from state 5 to state 6). Nevertheless, as the user of this transferred exergy from the steam is the process, it is charged with this ‘consumed exergy’, and the extraction method can be applied here. Then the additional equation is:

\[ c_5 = c_6 \]  
\[ (2.94) \]

The cost of the expended exergy in the process, \( c_p \), is determined by the process cost balance:

\[ c_5 B_5 = c_p B_p + c_6 B_6 \]  
\[ (2.95) \]

Table 2.10 presents the results given by the thermoeconomic analysis with both cost partition criteria.

As expected, the extraction method causes a higher value of the electricity generated in the steam turbine because this criterion charges this product with the turbine costs as well as the cost of the destroyed exergy inside the turbine. On the other hand, the exergy-based costs given by the equality method for electricity and exergy transferred to the process are the same, as a consequence of giving the same importance to both products.

The annual overall cost rate of the cogeneration plant is done by Eq. 2.96.

\[ C_{overall} = \sum_{\text{component}} C + c_{CH_4} B_{CH_4} = \text{US}\$4, 258,013/\text{year} \]  
\[ (2.96) \]

This cost rate must be distributed between both products of the plant: electricity and heat transferred to the process, according to the chosen cost partition criteria:

\[ C_{total} = C_{\text{electricity}} + C_{\text{heat}} \]  
\[ (2.97) \]
By the extraction method:

\[
C_{\text{total}} = 47.77 \cdot 8.5 \cdot 8,000 + 29.35 \cdot 4.3 \cdot 8,000 = 4,258,000/\text{year}
\]

By the equality method:

\[
C_{\text{total}} = 41.60 \cdot 8.5 \cdot 8,000 + 41.60 \cdot 4.3 \cdot 8,000 = 4,259,840/\text{year}
\]

The small difference of overall values is due to some approximations done during the calculations.

This study of a simple cogeneration plant evidences the importance of the thermoeconomic analysis in the determination of the utilities (process steam/heat and electricity) production costs, by means of using the concept of exergy as the basis to valuate each product of a given energy conversion plant.

Nevertheless, the useful information thermoeconomics can provide to a process analyst, it must be pointed out that it is simply one method of cost evaluation and not the panacea of the production cost methods. Even with the use of thermoeconomics, one is subjected to a given sort of arbitrariness due to the particular cost partition criteria chosen in the analysis.

### 2.6 Exergy and Renewability Analysis

In the last years, several discussions have been conducted about sustainable development, greenhouse gas emissions, environmental impact, and renewability of energy sources. However, until now, the concept of renewability has been associated to mass and energy balances, not taking into account the reduction of the quality of the energy (exergy destruction) related to energy conversion processes. The traditional definition of sustainability, that calls for policies and strategies that meet society’s present needs without compromising the ability of future generations to meet their own needs [23], does not provide a rational way to quantify this ability.
As stated by different authors [20, 26], exergy, which originates from the contrast between sun and space, drives flows of energy and matter on the surface of the Earth. This exergy input is destroyed in order to keep the natural cycles responsible for recycling materials in the surface, and a small part is stored as fossil fuels and mineral ores. Recycling takes time and exergy to be accomplished, but total recycling is not possible due to the second Law of Thermodynamics.

Currently, human development is based on the use of fossil fuels at a greater rate than that at which the deposit of fossil fuels have been generated. Also, since total recycling is not possible, it is imperative to seek for technologies that make better use of exergy available from all sources, including the so-called “renewable sources”. Thus, two aspects should be taken into account whenever discussing renewability of any product:

- Origin of its energy source;
- Efficiency of the energy conversion processes.

The use of the concept of reversible processes, the one that having occurred can be reversed to the initial system and surroundings states, in the analysis of the renewability of energy conversion processes can contribute to develop such analysis in a rational basis by using thermodynamic parameters.

Based on these aspects, one can define a renewability exergy index [25] that takes into account the exergy associated to the useful products of a given energy conversion process (or a set of processes), the destroyed exergy, the exergy associated to the fossil fuels required, the needed exergy to deactivate the wastes, and the exergy of by-products and not treated wastes, according to Eq. 2.98:

\[
\lambda = \frac{\sum B_{\text{product}}}{B_{\text{fossil}} + B_{\text{destroyed}} + B_{\text{deactivation}} + B_{\text{disposal}} + \sum B_{\text{emissions}}} 
\]  

(2.98)

where:

- \(B_{\text{product}}\) represents the net exergy associated to the products and by-products.
- \(B_{\text{fossil}}\) is the non-renewable exergy consumed on production processes chain.
- \(B_{\text{destroyed}}\) is the exergy destroyed inside the system, punishing the process for its inefficiencies.
- \(B_{\text{deactivation}}\) is the deactivation exergy for treating wastes, when they are carried to equilibrium conditions with the environment. It accounts for exergy required for passing the streams leaving the system, considered as wastes, to no harmful environmental conditions.
- \(B_{\text{disposal}}\) is exergy rate or flow rate related to waste disposal of the process.
- \(B_{\text{emissions}}\) is the exergy of wastes that are not treated or deactivated.

Depending on the value of the renewability exergy index, it indicates that:

- Processes with \(0 \leq \lambda < 1\) are environmentally unfavorable.
- For internal and externally reversible processes with non-renewable inputs, \(\lambda = 1\).
– If $\lambda > 1$, the process is environmentally favorable, and additionally, increasing $\lambda$ implies that the process is more environmentally friendly.
– When $\lambda \to \infty$, it means that the process is reversible with renewable inputs and no wastes are generated.

When $\lambda$ is higher than 1, the exergy of the products could be used to restore the environment to its conditions before the process and yet have a net output of exergy. In this sense, the natural cycles would only be responsible for the recycling of the renewable sources, considered as those able to be recycled by natural cycles without causing immediate harm to the environment in human lifetime basis.

A first application of the renewability exergy index is its determination for thermal power plants. For these systems, $\lambda$ is obtained as a function of the exergy efficiency of the power plant, taking into account that $B_{\text{deactivation}}$ and $B_{\text{disposal}}$ are zero, as shown by Eqs. 2.99, 2.100 (when a fossil fuel is utilized), 2.101 (when a renewable fuel is utilized) and Fig. 2.31, where it is shown the behavior of $\lambda$ with $\eta_b$ for both fuels.

$$\eta_b = \frac{W_{\text{net}}}{B_{\text{fuel}}}$$  \hspace{1cm} (2.99)

$$\lambda_f = \frac{W_{\text{net}}}{B_{\text{fuel}} + B_{\text{dest}} + B_{\text{fluegases}}} = \frac{\eta_b}{(2 - \eta_b)}$$  \hspace{1cm} (2.100)

$$\lambda_r = \frac{W_{\text{net}}}{B_{\text{dest}} + B_{\text{fluegases}}} = \frac{\eta_b}{(1 - \eta_b)}$$  \hspace{1cm} (2.101)

Note that, one can verify that, as stated before:

* $\lambda = 1$ when $\eta_b = 1$, for a reversible power plant using fossil fuel, and
* $\lambda \to \infty$ when $\eta_b = 1$, for a reversible power plant using renewable fuel

Considering that a conventional power plant using coal as fuel has thermal efficiency of about 35% for a Rankine subcritical plant and up to 50% for a
supercritical one, and that a combined cycle plant using natural gas can have thermal efficiency up to 60%, the $\lambda$ values for these types of power plants range from 0.18 to 0.43.

In case the supercritical power plant could operate with sugarcane bagasse as fuel (steam generate @ 600 °C and 294 bar, as it will be discussed in Chap. 6), the new value of $\lambda$ would be 0.38, for an exergy efficiency of 0.28 [14].

This result highlights that the renewability exergy index penalizes the use of fossil fuels as well as the inefficient energy conversion processes. Or, since $\lambda$ considers the exergy destruction in the energy conversion process, even if the exergy input comes from a so-called renewable source, an inefficient process jeopardizes the environmental performance of the energy conversion process. Also, an efficient energy conversion process with fossil exergy input may have an environmental performance even better than those with renewable sources, depending on the comparative values of exergy destroyed of the processes.

Finally, it is important to note that this index evaluates the renewability of a given energy conversion process and not a product. In this sense it is questionable the concept of renewable product usually employed to characterize energy sources and fuels.

References

1. Biot JB (1816) Traité de physique expérimentale et mathématique, tome 4, p 739, Paris, Deterville
References


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