First Principle:

Energy cannot be created or destroyed; it can only be converted into different energy vectors.

This sentence can be applied in practice to a generic system, having an overall energy level E_{sys}, whose variations must be balanced by energy transfers across the boundaries:

$\Delta E_{sys} + \Delta E_{cont} = 0$

The energy transfers across the boundaries can be of three different types:

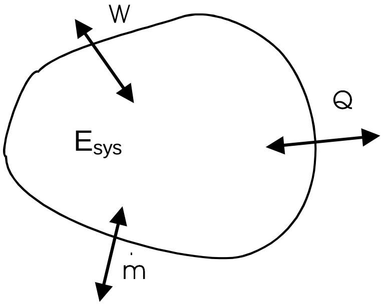


Figure 1 Generic system

a)Work transfer W
b)Heat transfer Q
c)Mass Transfer $\dot{m}$(Open systems)

For a system operating under cyclic conditions, the initial and final state are the same for all time intervals which are multiples of one cycle period. Consequently, the energy of the system $E_{sys}$is not changed and also the balance of mass transfers is closed at 0 (same initial and final mass).
These conditions apply also for time not exactly multiple of one period, provided that a significant number of cycles has been performed so that the energy balance can be closed with reasonable accuracy.

Consequently, as E_{sys} and the mass content of the system m_{sys} are not changed, the energy balance is closed with an equivalence between transfers of work and heat across the boundaries:

$$\Sigma Q + \Sigma W = 0 \qquad (1)$$

In Advanced Thermodynamics, considering also machine-learning applications, it is convenient to adopt a simple common rule for the sign of energy transfers, which applies to work, heat and mass:

Positive Sign: all quantities entering the system (arrow in)

Negative Sign: all quantities exiting the system (arrow out)

In practice this means that anything entering the system is increasing its energy level E_{sys}, while anything leaving the system is decreasing it.

As Eq. 1 was derived for cyclic conditions, in a generic thermodynamic property diagram x, y the initial and final system status can be labeled 1.

The cycle is composed of a continuous sequence of conditions; introducing the generic intermediate condition 2, passing to continuos transformations and splitting the cycle integral:

$$\oint (dQ + dW) = \int_1^2 (dQ + dW)_A + \int_2^1 (dQ + dW)_B = 0 \qquad (2)$$

Which means that the variable $\int_1^2 (dQ + dW)$ does not depend on the path – it is thus named a State Function.

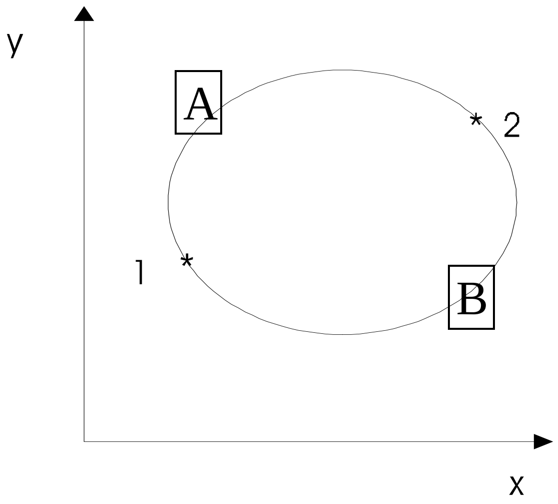


Figure2Cyclic process

This State Function is called Internal Energy U in the case of closed systems; for open systems in steady conditions, it is called Enthalpy H. These are the possible contributions to E_{sys}in terms of heat and work (Fig. 1).

Fig. 1 refers indeed to a generic system, which includes closed and open systems (mass transfer across the boundaries; variable volume of the system = moving boundaries):

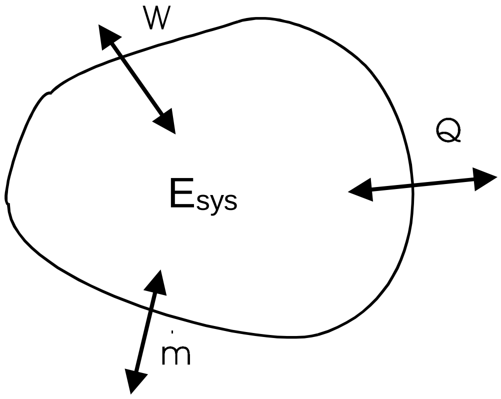


Figure1–
Generic system

Referring to Fig. 1, the energy balance (1st principle) can be now written detailing the two different contributions to E_{sys}:

$$\frac{dU}{dt} = \sum \dot{W} + \sum \dot{Q} + \sum \dot{m}h \qquad [W] \qquad (3)$$

Eq. 3 is written in terms of power units ([W]). Uis the overall Internal Energy(J) of the system, while his the specific Enthalpy(J/kg) which can be associated to each mass flow rate $\dot{m}$ (kg/s) entering (+) or exiting (-) the system.

Eq. 3 applies different rules for closed and open systems: this corresponds to the physical behavior of the system, which is respected automatically by the sign convention adopted: the unsteady energy level of the system (Internal Energy U)will be increased by any mass flow entering the system with specific enthalpy level h larger than that of the system; and decreased by any mass flow leaving the system (always, with specific enthalpy level larger than that of the system).

Eq. 3 shows that the Internal Energy U of the system is changing in time because of energy transfer across the boundaries (work, heat or mass); U is increased by positive (inward) fluxes.

Rigid Boundaries (including possible rotating shafts) do not allow the exchange of work (no displacement; work is the result of force*displacement; or, torque*rotation).

Adiabatic Boundaries do not allow the exchange of heat (infinite thermal resistance).

Impermeable boundaries do not allow the exchange of mass.

It is possible to define a new variable Transformation Energy [Borel and Favrat, 2010] allowing a compact notation:

$$\dot{E} = \sum \dot{m}h - \frac{dU}{dt} \qquad (4)$$

So that:

$$\dot{E} + \sum \dot{W} + \sum \dot{Q} + \dot{Q}_a = 0 \qquad (5)$$

In terms of power; or, at differential level:

$$dE + \sum dW + \sum dQ + d\,Q_a = 0 \tag{6}$$

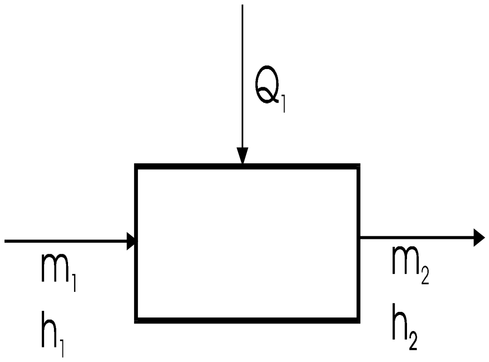
In Eqs. 5 and 6, one specific heat transfer term has been separated from the others, that is, Q_a – the heat transfered to the environment which is often disregarded and needs special attention; this term provides the link to the Second Principle of Thermodynamics.

Relevant simple cases – First Principle

All balances can be set automatically once the arrow sign is specified (+ in; - out).

1) Heat Transfer with an external source (thermal reservoir)

Open system in steady conditions; rigid boundaries, no work transfer; permeable boundaries (mass transfer; 1 = inlet; 2 = outlet); diabatic boundaries (heat transfer).



Continuity
(mass conservation):

$$\dot{m}_1 = \dot{m}_2 = \dot{m}$$

Energy conservation
(First Principle):

$$\dot{m}_1 h_1 - \dot{m}_2 h_2 + \dot{Q}_1 = 0 \qquad \dot{m}_1 (h_1 - h_2) + \dot{Q}_1 = 0$$

$$\dot{Q}_1 = \dot{m} \ (h_2 - h_1)$$

$h_2 > h_1$ $\quad \dot{Q}_1 > 0$ *given to the system (heating)*

$h_1 > h_2$ $\quad \dot{Q}_1 < 0$ *taken from the system (refrigeration)*

Relevant cases:

+ Solar collector[1]*; Nuclear reactor; Joule (resistance) heating;…*
- Heat loss from heat exchanger or building

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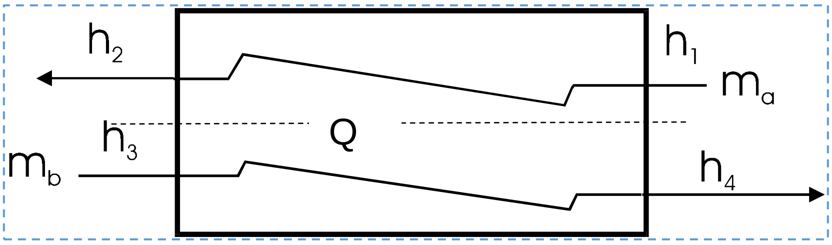
[1] Collettore_sol_2.ees

2) Heat exchanger (two streams)

This component is commonly called a Surface Heat Exchanger[2]*; indeed, the system is perfectly insulated and does not exchange heat with the surroundings; rather, its purpose is to transfer enthalpy from a hot (a= upper) to a cold (b = lower) stream.*
The enthalpy transfer (without further interactions – heat or work or mass) is only possible from a hot stream to a cold stream.

Open system, steady conditions (no storage of heat!), rigid boundaries (no work), adiabatic boundaries (no heat loss).



$W = 0$

$Q_e = 0$

Energy conservation (First Principle;1,3 in= +; 2, 4 out= -):

$$\dot{m}_a h_1 - \dot{m}_a h_2 + \dot{m}_b h_3 - \dot{m}_b h_4 = 0$$

That is, defining the heat $\dot{Q}$ *transferred between the two streams (dotted internal boundary):*

$$\dot{Q} = \dot{m}_a (h_2 - h_1) = \dot{m}_b (h_4 - h_3)$$

Usually the 4 streams are arranged in pairs with a counter-current scheme, which allows better performance. The solution can be generalized to heat exchangers with more than 4 streams applying the same rules. The solution applies also if one or both of the streams undergo a phase transition; however, in this case it is recommended to check that there is no pinch violation (locally negative temperature difference between the hot and cold stream).

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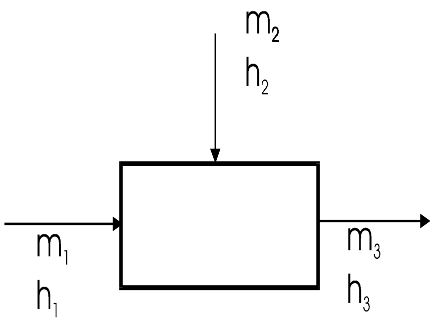
[2] HEGPMEX.ees; FEEDWATERHEATER.ees

3) Mixing heat exchanger (3 streams)

Open system, steady conditions (no storage of heat!), rigid boundaries (no work), adiabatic boundaries (no heat loss).



Continuity
(mass conservation 1,2 in= +; 3 out= -)

$$\dot{m}_1 + \dot{m}_2 - \dot{m}_3 = 0$$

Energy conservation (First Principle; 1,2 in= +; 3 out= -):

$$\dot{m}_1 h_1 + \dot{m}_2 h_2 - \dot{m}_3 h_3 = 0$$

The system is equivalent to a 4-stream co-current surface heat exchanger (case 2), where the two exiting streams exit at the same conditions (zero temperature difference).

The solution corresponds to a simple mixing node; it can be generalized to a larger number of streams (inlet and outlet), or to a bifurcation – 2 stream out, 1 in).

Relevant cases:

- *Simple mixing temperature controller (shower, building heating systems)*
- *MFH*[3] *(Mixing Feedwater Heater) in steam power plants*
- *Gas Turbine film cooling (combustor, nozzles, blades,…)*

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[3] MFH.ees; DEGA_VAP1.ees

4) Work components (Turbines, compressors,…)

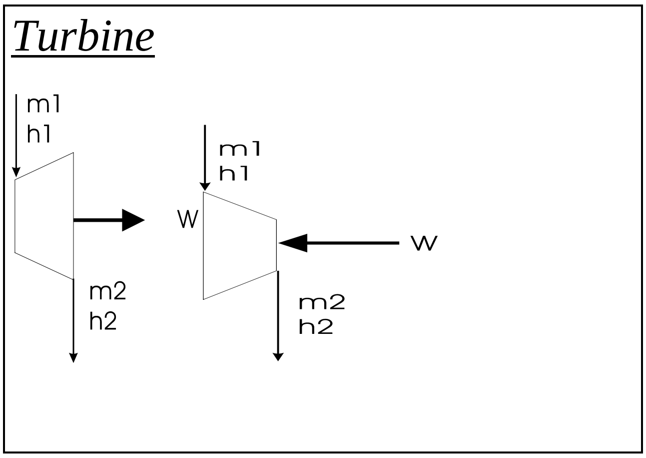
Open system, steady conditions, adiabatic[4] boundaries (no heat loss). Components dedicated to work. Assume 1 = inlet; 2 = outlet in all cases.

$$\dot{W} + \dot{m}\ (h_1 - h_2) = 0$$

$$\dot{W} = \dot{m}\ (h_2 - h_1)$$

$\dot{W} < 0$ *Turbine* *(output work)*

$\dot{W} > 0$ *Compressor* *(input work)*



Final Notice (1st principle): examples 1, 2 and 4 show how the effect to be evaluated is often the variation of enthalpy; if positive (+) this represents heat or work spent to obtain this effect; if negative (-) this represents useful output of the system (in terms of heat or work respectively.Please remember that when it comes to defining a process efficiency or an useful outcome, these matters are not directly linked to a flow in or out or an arrow sign. This requires human insight, or at least some human-oriented machine learning (that is, definition of rules for "fuels" and "products").

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[4] There are relevant cases of non-adiabatic work components: cooled gas turbines, "warm expanders" with significant wall heat transfer, "Fanno" expanders where friction losses play a relevant role in terms of working fluid equivalent heat transfer; also, condensing/evaporating flows in turbines or compressors…. These cases can be treated separating effects (work and heat) and introducing pre- or post- cooling/heating, provided that reliable heat transfer correlations are available.

The Carnot engine

The Carnot theorem states that, among all engines operating in cyclic mode between two assigned heat reservoirs[5], the maximum efficiency is achieved by the machine operating under internally and externally reversible mode; in fact, any dissipative effect is absent for such a machine.

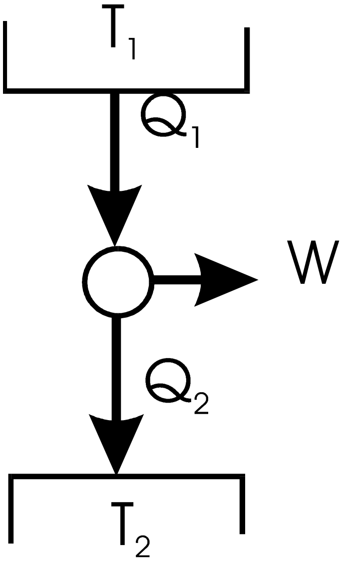

Figure 3 –A machine operating between two reservoirs

Efficiency for an engine producing work is defined as the useful effect (Work W) divided by the input heat Q_1 exchanged with the upper (hot) reservoir; applying the First Principle under cyclic conditions:

$$\eta_c = W_{max}/Q1 = 1- Q_{2min}/Q1 \qquad (7)$$

As, in general (for cyclic conditions):

$$Q_1 - Q_2 - W = 0 \qquad \text{(first principle)}$$

---

[5] Heat Reservoir = system with ∞ Heat Capacity [W/K]

Its temperature does not change as a consequence of heat transfer (in or out).

Thus, it can bestated that:

The system producing maximum work when interacting with two thermal reservoirs is also the one which minimizes the heat discharged to the cold reservoir (usually, the environment).

No assumption was done relating to the type of fluid; the system interactions with the two reservoirs must then be represented by one single variable; it is convenient to call this variable Thermodynamic Temperature (in short: **Temperature**). As the functional law is arbitrary, it is very convenient to choose a linear dependence[6] (efficiency vs. temperature), so that (for a reversible engine):

$$\eta_C = W_{max}/Q_1 = 1- Q_{2min} /Q_1 \quad = 1- T_2/T_1 \tag{8}$$

Eq. 8 is important to introduce a new thermodynamic variable, named Entropy; in fact, for such a reversible engine:

$$Q_2/T_2 = Q_1/T_1 = \Delta S \tag{9}$$

(the entropy variation of the two reservoirs is the same).

The Carnot theorem is very important but it is restricted to a very specific class of processes: reversible processes operating between two reservoirs. Here, it was recalled only to introduce the Thermodynamic Temperature (and, subsequently, Entropy).

A Thermodynamic reservoir is defined as a system with infinite heat capacity: in other terms, its temperature will not change independently of the heat subtracted or supplied to the reservoir.

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[6] Indeeed the linear dependence allows an easy experimental lab fit knowing two reference points; this was done for a common substance (water) referring to points of good repeatability (phase change solid/liquid and liquid/vapor). The Celsius scale divides the interval in 100 sub-intervals (°C), asusming 0°C for solid/liquid transition and 100°C for liquid/vapor (just controlling atmospheric pressure, which should be the reference 101,325 kPa).

In nature, there are systems which can be assimilated to reservoirs, as they have very large heat capacities: for example, radiation from the sun, or the surrounding environment (for example, atmosphere or the oceans). This applies to systems of engineering relevance, where time scales are measured in terms of second, minutes or hours.

A relevant technical case of a system of infinite heat capacity is related to phase change processes, which allow to supply or subtract heat at constant temperature; however, this is true to a limited extent (in practice, until complete phase transition is achieved).

Systems with finite thermal capacity

In engineering practice, we are often called to optimize systems with finite heat capacity: that is, systems (not reservoirs) where when you subtract heat, the temperature is diminished; and, if you provide heat, temperature is raised.

Specific relevant cases of limited heat capacity are linked to heat recovery situations: for example, from solar collectors, from waste heat streams (industrial; combustion gases from gas turbines, reciprocating engines,….), rom geothermal resources,...

The**Heat Capacity [W/K]** is actually defined as the product of mass flow * specific heat (for an open system, constant-pressure specific heat): $C = \dot{m} \cdot c_p$. Heat Capacity represents a common thread along this course of advanced thermodynamics (from energy to exergy and pinch analysis). MSc level students must become accustomed to treating these problems (analysis and optimization), while typically only thermodynamic systems with infinite heat capacity (reservoirs) at treated at BSc level.

Optimization of Energy Systems under the constraint of limited heat capacity requires further skills than the simple rules of the Carnot Engine. However, there is one important heat transfer process which usually takes place interacting with a reservoir, that is, discharge of heat to the environment. This is the reason why special evidence was given to the term Q_a in Eqs. 5-6. It should also be considered that usually this specific heat transfer term (to the environment) does not happen in a reversible mode – that is, some temperature difference with respect to the conditions of environment are necessary in real systems. In any case, the amount of heat discharged to the environment should be kept as low as possible, so that the energy conversion system is able to convert as much as possible of the high-temperature heat interaction into useful work.

In practice, the Carnot cycle cannot be considered a reference in general; it maintains its optimization features only in the very special case of thermal interaction with two isothermal reservoirs (infinite heat capacities).

Entropy

From the point of view of thermodynamics, Entropy can be introduced as a state function; Clausius postulated its existence, and defined it with reference to a reversible transformation, in differential form, as the ratio dQ/T.

The Clausius theorem states that for a reversible cycle:

$$\oint dQ / T = 0 \qquad (9)$$

Or, in discrete formulation considering a series of heat transfer processes:

$$\sum_i Q_i / T_i = 0 \qquad (10)$$

The fact that $\oint dQ/T=0$ is a sufficient condition for stating that $dQ/T$is a state function, because it does not depend on the specific transformation path followed but only on the initial and final states of the system.This is however true only for a series of reversible transformations; introducing irreversibilities, entropy cannot be conserved and this is treated introducing the system entropy balance.

Entropy balance

Entropy as a state function is associated with heat transfer processes at differential level dQ; considering that it is a state function, it is possible to write its balance following the same steps as for Energy. The result is:

$$dS/_{dt} = \sum_i \int {}^{dQ_i}/_{T_i} + \sum_j m_j s_j + {}^{dS_{irr}}/_{dt} + {}^{Q_a}/_{T_a} \quad (11)$$

where

- S is the overall entropy of the system (varying in time) (in J/K)
- $M_j s_j$are the entropy flux terms (positiveif entering the system, negativeif exiting)
- dQ_i/T_iexpresses the entropy variation due to the i-th heat transfer processacross the boundaries, taking place at temperature T_i; this is kept as a differential term under an integral sign (extending along the heat transfer process transformation), because temperature can be varying during the process (no reservoirs now!).As usual, a positive sign results if the system is heated (heat in), a negative if it is cooled (heat out).

- $Q_a/T_a$is the same heat transfer term explicitly dedicated to reversible heat transfer with the surrounding environment (whose temperature T_a is not changing – the environment is considered as a heat reservoir)
- $dS_{irr}/dt$is a specific term, which is always positive, accounting for internal and external irreversibilities taking place in the system. Irreversibilities can only augment the entropy of the system; this term allows closure of the balance, which – opposite to the Energy balance – is not set in terms of conservation. Indeed Entropy is not conserved, but it is always augmented as a consequence of real, irreversible processes. For example, friction can be considered equivalent to supplying heat to the system. However, it is possible to decrease the entropy of the system- for example, by simply cooling it, or subtracting mass from it.

Consequently, it is correct to say that real (irreversible) processes always increase the entropy of the system. It is wrong to say – in general – that entropy of the system can only increase (we can decrease it by cooling, or extracting mass from the system).

However, when considering the extended system composed of the original system + the environment, it is correct to say that the overall entropy can only increase (decreasing the entropy of the system implies that this entropy is transferred to another system, or finally to the environment; as this is usually done by means of real, irreversible processes, the overall entropy of the extended system can only increase).

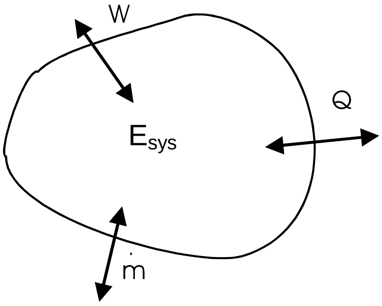
Availability balance

A relevant extension of the first and second principle can be obtainedmultiplying the entropy balance (11) by T_a, and subtracting the resulting equation from (5):

1st principle (Energy conservation):

$$\sum \dot m h - \frac{dU}{dt} + \sum \dot W + \sum \dot Q + \dot Q_a = 0 \tag{5}$$

$$\left(\dot E = \sum \dot m h - \frac{dU}{dt} \right) \tag{4}$$



2nd principle (entropy balance):

$$dS/dt = \sum_i \int d\dot Q_i / T_i + \sum_j \dot m_j s_j + dS_{irr}/dt + \dot Q_a / T_a \tag{11}$$

That is:

$$-\sum_i \int d\dot Q_i / T_i - \sum_j \dot m_j s_j - dS_{irr}/dt + dS/dt - \dot Q_a / T_a = 0$$

Multiplying (11) by T_a:

$$-T_a \sum_i \int d\dot Q_i / T_i - T_a \sum_j \dot m_j s_j - T_a dS_{irr}/dt + T_a dS/dt - \dot Q_a = 0$$

… summing to (5), the term Q_a is canceled, yielding:

$$\sum_k W_k + \sum_i \int (1 - T_a/T_i) dQ_i + \sum_j m_j (h_j - T_a s_j) - d(U - T_a S)/dt - T_a dS_{irr}/dt = 0 \tag{12}$$

This is called the System Availability Balance.

Within the system availability balance, specific terms can be identified:

1) $(1-T_a/T_i) = \theta_i$Carnot *Factor*; also called non-dimensional thermodynamic temperature, it corresponds to the efficiency of a Carnot engine operating between the temperature level $T_i$of the heat transfer process and the environment temperature T_a.

2) $U - T_aS=A$ *Availability function for closed systems*

3) $h - T_as = b$ *Availability function for open steady-state systems*

4) $L=T_a\ dS_{irr}/dt$ Rate of availability destruction *of the system* (also called *rate of exergy destruction*, or *flux of anergy*); this is always a *positive contribution*.

As was done for the*Transformation Energy* (4), it is possible to define a generalized Availability Functionwhich can be appliedto both closed and open systems:

$$\Xi = \sum_j m_j(h_j - T_a s_j) - \frac{d}{dt}(U - T_a S) \tag{13}$$

Allowing the compact notation of the Availability balance:

$$\sum_k W_k + \sum_i \int (1 - T_a / T_i) dQ_i + \Xi - T_a\, dS_{irr} / dt = 0 \tag{14}$$

Exergy (of transformation: state function)

The Transformation Exergy can be obtained from availability by simply subtracting the availability in reference state conditions:

$$X = A - A_a = (U-U_a) - T_a(S-S_a) \qquad [J] \qquad (15)$$

which is valid for closed systems; for open systems in steady state, a specific (flow) availability can be defined as:

$$x = b - b_a = (h-h_a) - T_a(s-s_a) \qquad [J/kg] \qquad (16)$$

The *Transformation exergy*isan "extrinsic" state function (it depends on the conditions at the *Reference State*).

The Reference State in thermodynamics is set at T_a = 298.16 K (25°C) and p_a = 101325 Pa (1 bar). A system under these conditions is called in *thermo-mechanical equilibrium with the environment*. When the system is in *thermo-mechanical equilibrium with the environment*, it cannot produce work interacting physically with the surrounding environment. More extensive equilibrium conditions with the reference environment can be set if the system chemical components are exactly the same as those of the reference environment (*Thermo-Chemical Equilibrium with the environment*).

Exergy is an indicator of the capaciy of a system, of a matter stream flow or o fan Energy interation (heat, work, potential or kinetic energy) to produce work when interacting with the reference environment.

In case of a fully-reversible process, the work obtained is maximized and its value is equal to the original level of exergy.

What was introduced up to now holds for non-reactive systems; an extension to reactive systems can be done through the introduction of chemical exergy – which requires a definition of the reference environment in terms of the complete chemical composition.

Restricting to non-reactive systems, the change of exergy between two thermodynamic conditions 1 and 2 is exactly equal to the change of availability (contributions A_a o b_a cancel when subtracting for the two states); this change of exergy between the two thermodynamic statesis the maximum work obtainable leading the system from state 1 to state 2.

$$\boxed{\sum_k W_k} + \boxed{\sum_i \int (1 - T_a / T_i) dQ_i} + \sum_j m_j (h_j - T_a s_j) - d(U - T_a S)/dt - T_a dS_{irr}/dt = 0 \qquad (12)$$

Eq. 12 shows that there are other contributions to exergy, different from transformation exergy; these are listed and discussed in the following:

Work Exergy is exactly equal to mechanical work.

Heat Exergy is accounted by the term: $\theta_i Q_i = (1 - T_a / T_i) Q_i$and is equal to thework W_{max} which wouldbe produced by a fully-reversible cycle operating between temperature levels T_i and T_a. The Carnot Factor $\theta_i$provides a precise measure of the quality of the heat transferred Q_i considering the temperature level at which it is available.

It is important to consider the trend of θas a function of temperature T_i ; this is shown in Figure 4. The slope of the curve becomes large when approaching low temperatures (refrigeration/cryogenic fields of application).

As a matter of fact, subtracting heat becomes more and more difficult with decreasing temperature (that is, more work is necessary for the same amount of removed heat); for this reason, it is not surprising that the early applications of exergy (1960-1970) were devoted to the field of refrigeration and cryogenic processes (e.g., Ammonia synthesis, production of liquid oxygen and nitrogen, natural gas liquefaction,…). In these extreme cases, only minimization of irreversibilities (often through extensive and accurate regeneration) allows to develop a functional process.

For energy conversion and utilization processes, matters are simpler but the search for more efficient processes has led scientists since the middle 70s to apply exergy concepts. In this case, heat is often provided at relatively high temperature by combustion of a fuel; or, it can be available from renewable resources (such as solar, or geothermal). Consequently, it is recommendable to consider the following:

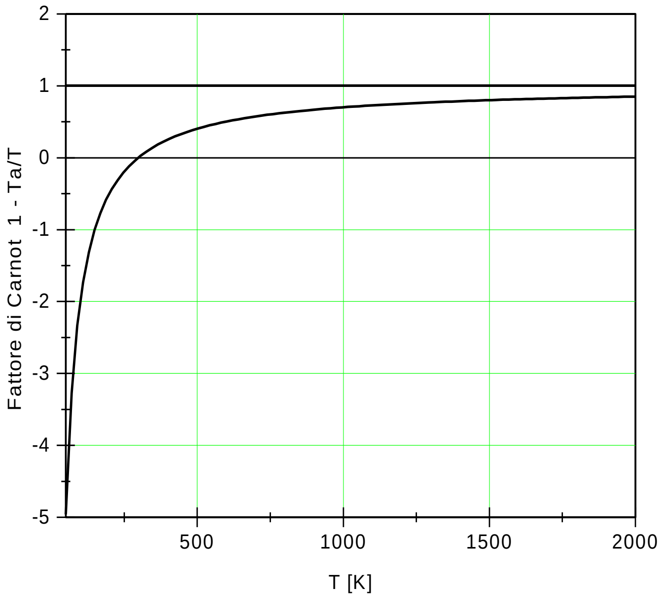


Figure 4 – Carnot Factor vs. temperature

a) as $T \to \infty$ $\theta \to 1$

Heat exergy becomes equal to the heat exchanged

b) $0<\theta<1$ in the range $T_a< T <\infty$.

c) when $T = T_a$,

$\theta = 0$. The heat exergy cannot be converted into work (thermal equilibrium with the environment)

d) when $0< T <T_a \theta<0$. θ becomes rapidly lower than -1 (at 135K = -135 °C) ; θ = - 2 is reached at about 90K. In comparison, the range Δθ = 1 needed a temperature change from ∞ to 25°C for Energy conversion (over-environment temperature) applications.

As a result, θ is the correct instrument to assess the quality of heat according to its temperature level.

For non-reactive systems, exergy or availablity analysises are equivalent; **for reactive systems, an estended formulation of exergy is necessary, providing a common reference for different substances.**

Entropy-mean temperature

As stated before, thermodynamic reservoirsare not common in the real environment, where a temperature decrease is the normal result of heat subtraction (and viceversa).

This is the reason why the term T_i was kept under an integral sign when dealing in Eq. 12 with transformations involving the transfer of heat: $T_i$is actually changing during the transformation.

It is however possible to define an equivalent average temperature T_{mi} allowing to get ridof the integral sign (as for the other terms of Eq. 12). In order to do that, we can define the Carnot Factor corresponding to this average temperature:

$$\theta_{mi} Q_i = (1 - T_a / T_{mi}) Q_i = \int (1 - T_a / T_i) dQ_i \quad (17)$$

It can be easily seen that the correct way of averaging isan entropy-mean average. The Entropy-Mean temperature T_m is defined from the equality:

$$Q_{AB} = \int_A^B dQ = \int_A^B T ds = T_m \int_A^B ds = T_m (s_B - s_A)$$

That is:

$$T_m = Q_{AB} / \int_A^B ds = Q_{AB} / \boxed{\int_A^B dQ / T} \qquad (18)$$

If the Carnot Factor is calculated using T_m:

$$\theta_m = (1 - T_a / T_m) \qquad (19)$$

The use of this (Entropy-Averaged) Carnot Factor is equivalent to maintaining the integral formulation, as results from the following passages:

$$\int_A^B \theta dq = \int_A^B (1 - T_a / T) dq = Q_{AB} - T_a \boxed{\int_A^B dQ / T} =$$
$$Q_{AB} - (T_a / T_m) Q_{AB} = Q_{AB} (1 - T_a / T_m) = \theta_m Q_{AB} \qquad (20)$$

The Entropy averaging process can be substituted by a log-mean averaging only for ideal processes where specific heat is not changing along the process. This is true for ideal gases, where:

$$ds = c_p \frac{dT}{T} - R \frac{dp}{p} \quad (21)$$

$(\frac{dp}{p} = 0 \text{ for steady state open system} = \text{heat transfer process})$

And for liquids, where:

$$ds = c \frac{dT}{T} \quad (22)$$

However, in many processes of technical interest (depending on the working fluid), c_p or c undergo relevant variations with temperature, so that the original entropy-averaging approach is recommended. The same holds if a part of the heat transfer process takes place with a phase transition ($c \rightarrow \infty$); in these cases, the process should be split (part of heat transfer is taking place at constant temperature), as happens in evaporators or condensers.

Equivalence: exergyand entropy analysis

Entropy analysis was already applied by researchers arriving to similar results as for exergy analysis. The following compares the two methods, and shows that exergy analysis is more straightforward and has a larger potential for systematic application development.

Dealing with Energy conversion systems, the production of work is analyzed using Energy or Exergy balance, referring (a) do the ideal (reversibile) case (b) to the real (irreversibile) case. In all cases the system undergoes the same transformations of heat transfer (with the notable exception of heat transfer with the environment Q_a) and has the same intial and final states:

Real System:

Energy balance

$W^- = \Sigma_i Q_i + \Sigma E_l - Q_a$

Exergy Balance

$W^- = \Sigma_i \theta_{mi} Q_i + \Sigma_l \Xi_l - L_x$

Ideal system (no irreversibilities, $L_x=0$):

Energy balance

$W^-_{max} = \Sigma_i Q_i + \Sigma E_l - Q_{a\,min}$

Exergy Balance

$W^-_{max} = \Sigma_i \theta_{mi} Q_i + \Sigma_l \Xi_l$

Subtracting the first from the second equation in each of the squares:

$$W^-_{max} - W^- = Q^-_a - Q^-_{a\,min} = L_x > 0 \qquad (23)$$

The Exergy Destruction L_x is equal to the decrease of capacity of producing work, with respect to the maximum work conditions which are obtained in fully reversible conditions.

From the point of view of the Energy balance, the same decrease of capacity of producing work appears asan increase of the heat discharged to the environment (real case vs. ideal case).

This increase of heat discharge to the enviroment can be represented as:

$$Q^-_a - Q^-_{a\,min} = T_a \Delta S_{irr} = L_x > 0 \qquad (24)$$

which definitely states the equivalence between the two approaches; in fact, the Entropy Analysis is based on the evaluation of the cumulative effect of irreversibilities, resulting in the overall increase of Entropy ΔS_{irr} of the system, determined by the several processes involved (this includes internal and external irreversibilities); multiplication of ΔS_{irr} by $T_a$gives the augmented heat discharge of the system when operating in real conditions, compared to the base value which would be achieved in fully reversible conditions; this is also equal to the decreased work capacity.

Eq. 24 states that the term L_x(Exregy Destruction), which is equivalent to the additional heat realease to the environment due to the presence of irreversibilities, can be represented in a thermodynamic state diagram T- s with the area of a rectangle having height $T_a$and base Δs_{irr}. This property[7] will be utilized in the following treatment of components cases which have already been analyzed in terms of Energy balance.

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[7] Introduced by Ahern, The **Exergy** Method of Energy Systems Analysis , Wiley, 1980

Examples – Exergy Analysis (Non-Reactive Systems)

1) Heat Transfer with an external source (thermal reservoir)

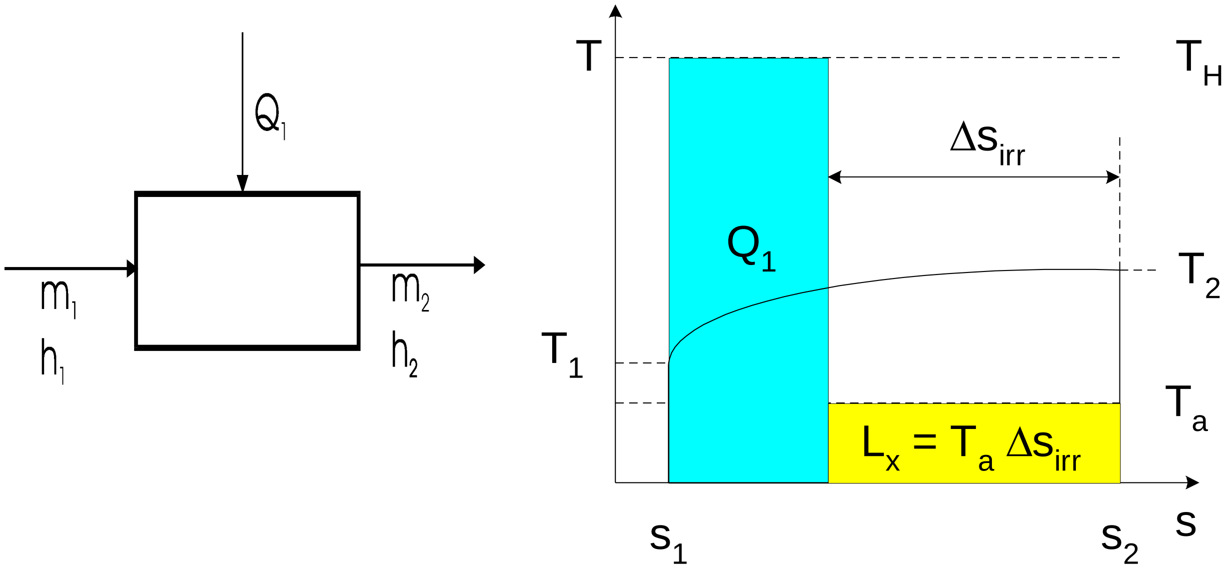

Figure 5 – Heat transfer with external source

$$m\,[\,(h_1 - h_2) - T_a(s_1 - s_2)] \quad + Q_1\,(1 - T_a\,/\,T_H\,) = L_x$$

Energy conservation(First Principle): $Q_1 = m\,(h_2 - h_1)$

$h_2 > h_1$ $\quad Q_1 > 0$ $\quad$ *given to the system (heating)*

Exergy Balance:

$$L_x = T_a\,[m\,(s_2 - s_1\,) - Q_1/T_H] = T_a \Delta S_{irr}$$

Relevant cases:
+ Solar collector[8]*; Nuclear reactor; Joule (resistance) heating;…*
- Heat loss from heat exchanger or building

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[8] Collettore_sol_2.ees

2) Heat exchanger (two streams)[9]

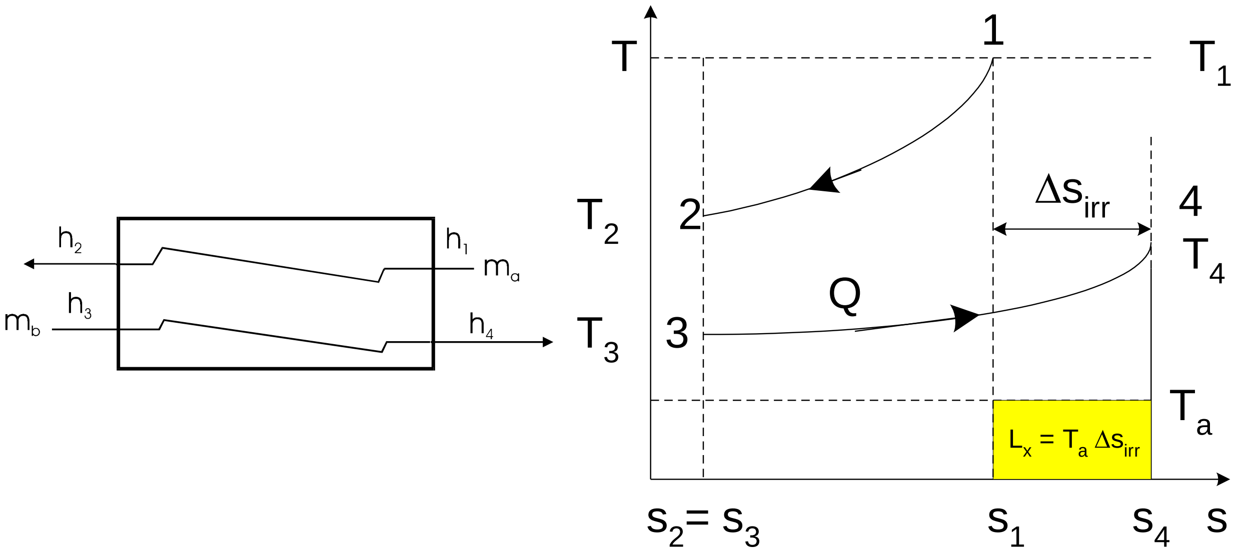

Figure 6 – Surface Heat Exchanger

Energy conservation (First Principle;1,3 in= +; 2, 4 out= -):

$$m_a h_1 - m_a h_2 + m_b h_3 - m_b h_4 = 0$$

That is: $Q = m_a (h_2 - h_1) = m_b (h_4 - h_3)$

Exergy Balance:

$$L_x = \{ m_a [(h_1 - h_2) - T_a(s_1 - s_2)] - m_b [(h_3 - h_4) - T_a(s_3 - s_4)] \}$$

$$= T_a [m_b (s_3 - s_4) - m_a (s_1 - s_2)] = T_a \Delta S_{irr}$$

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[9] HEGPMEX.ees; FEEDWATERHEATER.ees

3) Mixing heat exchanger (3 streams)[10]

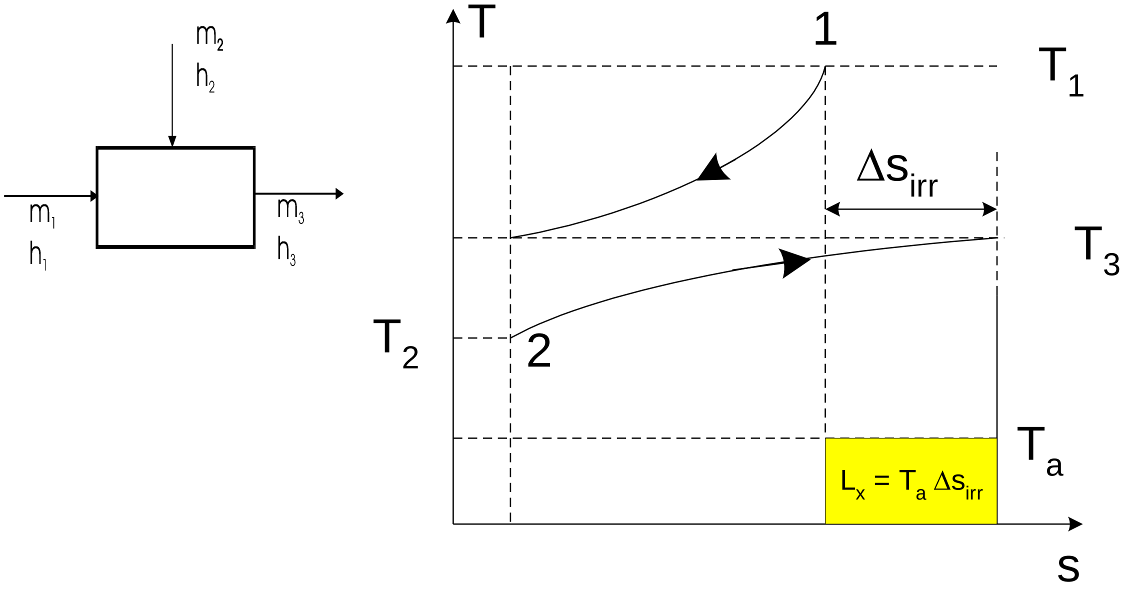

Figure 7 – Mixing heat exchanger

Continuity(mass conservation 1,2 in= +; 3 out= -)

$$m_1 + m_2 - m_3 = 0$$

Energy conservation (First Principle; 1,2 in= +; 3 out= -):

$$m_1 h_1 + m_2 h_2 - m_3 h_3 = 0$$

Exergy Balance:

$$L_x = [\, m_1 \,(h_1 - T_a s_1) + m_2 \,(h_2 - T_a s_2) - m_3 \,(h_3 - T_a s_3)\,]$$

$$= T_a \,(m_3\, s_3 - m_1\, s_1 - m_2\, s_2) = T_a \Delta S_{irr}$$

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[10] MFH.ees; DEGA_VAP1.ees

4) Work components (Turbines, compressors,…)

Energy conservation (First Principle; 1 in= +; 2 out= -):

$W + m\,(h_1 - h_2) = 0 \qquad\qquad W = m\,(h_2 - h_1)$

$W < 0$	*Turbine*	*(output of the system)*	$h_2 < h_1$
$W > 0$	*Compressore*	*(input to the system)*	$h_2 > h_1$

Exergy Balance:

$$W + m\,[(h_1 - T_a s_1) - (h_2 - T_a s_2)] = m\,[T_a(s_2 - s_1)] = T_a \Delta S_{irr}$$

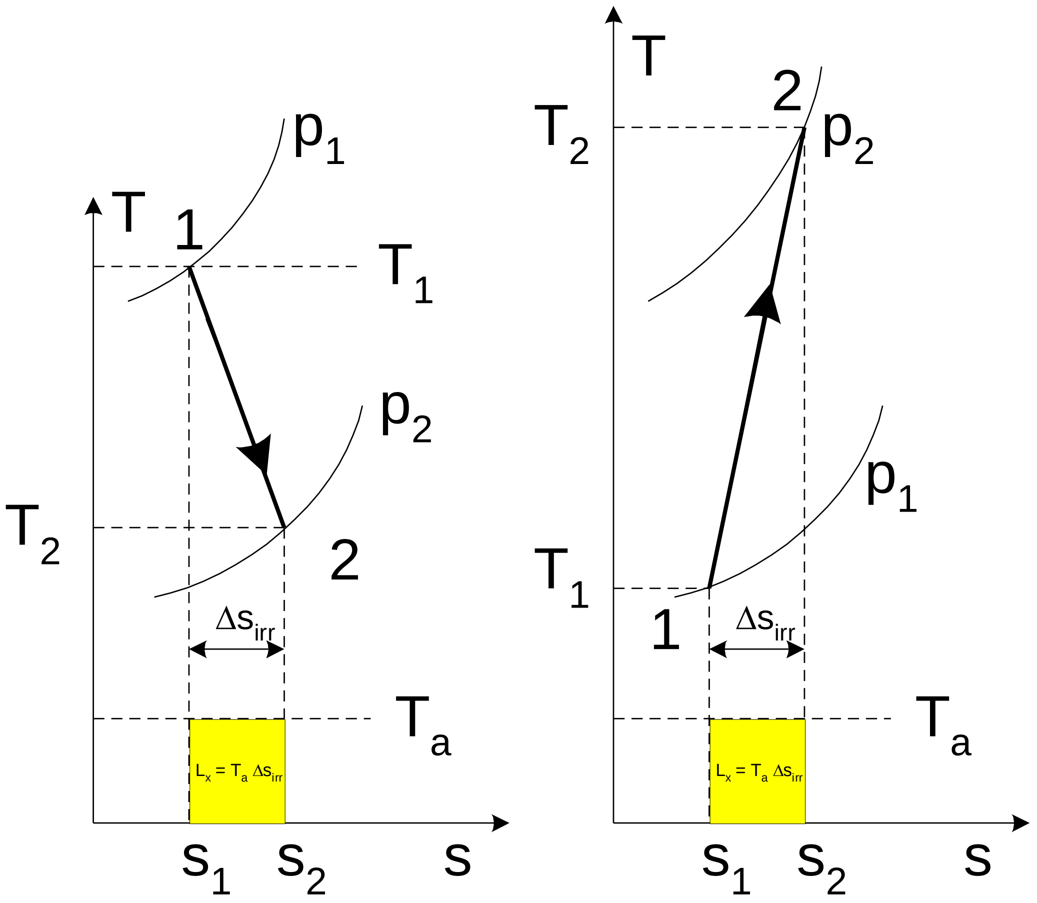

Figure 8 – Turbine (left), Compressor (right)

Exergy/availability balance and Exergy Efficiency

The exergy/availability balance (12) can be rewritten separating input (+) and output (-) terms:

$$\Sigma_k W^- + \Sigma_i \theta_{mi} Q_i^- + \Sigma_l \Xi_l^- = \Sigma_k W^+ + \Sigma_i \theta_{mi} Q_i^+ + \Sigma_l \Xi_l^+ - \Sigma_h L_{xh}$$

(25)

Now the exergy destruction L_x is shown decomposed into different contributions, originating locally in the several plant components. Eq. 25 allows to define the Exergy Efficiency as the ratio of (exergy obtained)/(exergy spent):

$$\eta_{xd} = (\Sigma_k W^- + \Sigma_i \theta_{mi} Q_i^- + \Sigma_l \Xi_l^-)/(\Sigma_k W^+ + \Sigma_i \theta_{mi} Q_i^+ + \Sigma_l \Xi_l^+)$$

(26)

In Eq. 26η_{xd} is actually the **Direct Exergy Efficiency** (output/input); but Eq. 25 can be used to derive the **Indirect Exergy Efficiency**, considering that the output exergy is equal to the input exergy minus the exergy destructions; thisis much more useful asit allows toput in evidence the individual contrbutions of each plant component:

$$\boldsymbol{\eta_{xi} = 1 - (\Sigma_h L_{xh})/(\Sigma_k W^+ + \Sigma_i \theta_{mi} Q_i^+ + \Sigma_l \Xi_l^+)} \qquad (27)$$

In Eqs. 26 and 27 the outputs or inputs of exergy can be of very different nature: work, heat exergy, transformation exergy. Indeed the need for exergy analysis applied to energy conversion systems was fostered by the necessity to correctly evaluate multi-product systems: for example, CHP (Combined Heat and Power) or Tri-generation (CHPC Combined Heat Power and Cold), but also systems integrating power/heat/cold production with that of chemicals (biofuels, intermediate chemical products) which can represent powerful energy storage solutions. Exergy analysis is in these cases fundamental, because it allows a correct thermodynamic evaluation of the multi-product process, and paves the way to a correct evaluation of the buildup of the cost of different products (thermo-economics or – better – Exergo-economics).

Exergy Destruction and Exergy Loss

In Eq. 27, the term $\boldsymbol{\Sigma_h L_{xh}}$ must be reconsidered to include not only Exergy Destructions, but also Exergy Losses. The Exergy Loss represents a direct dissipation of exergy (for example work, heat exergy, or transformation exergy linked to a material stream) through its discharge to the environment.

Examples of Exergy Losses are heat dissipation to the environment in heat exchangers with non-ideal insulation; discharge of hot gases (e.g. stacks, gas turbine exhausts) or condensers of power plants or refrigeration units. In many cases these represent unavoidable losses, with reference to components having the function of interaction with the environment (e.g. stacks, condensers,…). These heat or sensible heat release streams do not actually take place under equilibrium conditions with the environment, are irreversible and represent thus an exergy loss.

Some components (e.g. heat exchangers, condensers, solar collectors,…) have both an Exergy Destruction and an Exergy Loss.

It is important to differentiate Exergy destruction from Exergy Loss[11]. The following are the general correct definitions:

- **Exergy Destruction E_D**is a result of component irreverisbilities (internal and external), which cannot approach the ideal (reversibile) operation. This means that the component conserves energy, but introduces its progressive degradation with its transformation (e.g.: heat transferred from higher to lower temperature level; heat transformed in work; chemical Energy transformed in electricity, heat or work). The recent developments of Advanced Exergy Analysis add a classification of the component exergy destruction into endogenous (internalto the component) orexogenous (produced in the specific component as a result of inefficiencies in other plant components). As many energy conversion systems involve the presence of loops (regeneration, or recovery of material streams) there also exists a mesogenous contribution (exergy destruction produced by the component, because of the resulting effects of its inefficiencies over the other plant component which determine a further contribution to the endogenous destruction).

- The **Exergy Loss E_L**is always associated directly with waste of Energy to the environment (e.g.: lack of insulation in heat exchangers or engines;discharge of streams with non-zero energy; direct wasted work). From the economics point of view, when the loss is functional to the system operation[12], it is not attributed to the component, but it is accounted to the system as a whole.

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[11] Not all schools apply this important rule. Here we refere to the Bejan-Moran-Tsatsaronis Wiley 1996 book approach, which is the reference.

[12] Discharge of heat to the environment in place of the “cold reservoir”; discharge of combustion gases substituted by fresh air+fuel input stream;…

System application (steam power plant)

The following system application (Figure10) deals with an elementary steam power plant, and is solved showing also a graphical interpretation of exergy destructions and losses. Exergy destructions are all represented by rectangles having height T_a ($L_x = T_a \Delta S_{irr}$); instead, Exergy Losses are rectangles lying over the T_a line.

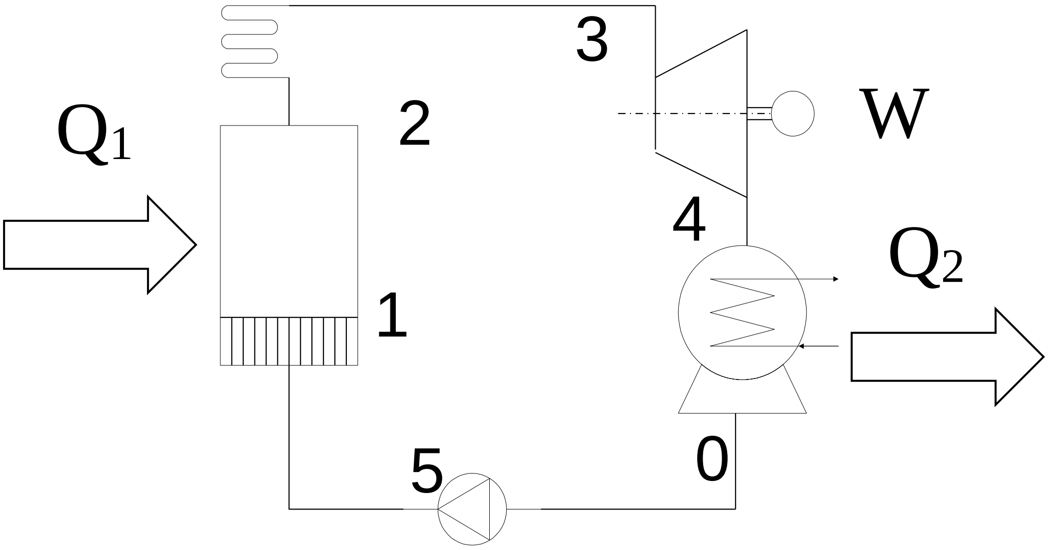

Figure 10 – Elementary steam power plant

The input exergy is assimilated to the chemical exergy of the fuel, approximated by it lower Calorific Value. This is transformed into heat in the heat generator (boiler), with an efficiency η_b (all heat generators have non-perfect insulation and present a stack discharge loss):

$$Q_1 = m_c \eta_b \, HCI \qquad \text{(SPP.1)}$$

Exergy loss of the steam generator:

$E_{L1} = m_c\, HCI\, (1- \eta_b)\, (1- T_a/T_H)$ (SPP.2)

Ideally, chemical exergy could be converted in Q_1 at infinite temperature; in practice, the limiti s set by the adiabatic combustion temperature T_H shown in the figure.
Q_1 would be represented in the T-s diagram by the complete area below T_H.
The exergy loss is equivalent to heat dispersed at T_H, fiven by Eq. SPP.2; graphically, it is represented by the cyan area shown in Figure 11.

Exergy destruction in steam generator heat transfer
It can be treated globally as follows, considering the complex of economizer, evaporator and supeheater, giving rise to a contribution of the type seen for heat exchangers ($T_a \Delta S_{irr}$):

$E_{DHT} = T_a\, (S_3 – S_B)$ **(SPP.3)**

The corresponding box area is shown in Magenta in Fig. 11.

Exergy destruction due to friction losses in the steam generator
Friction produces a total pressure loss, which is treatetd assuming that it takes place at the end of the heat transfer process[13];this loss can be represented again as a $T_a \Delta S_{irr}$, with ΔS_{irr} easily calculated using the total pressure/entropy functional dependence (or steam tables, assuming $h_3 = h_{3'}$)

$E_{DF} = T_a\, (S_{3'} – S_3) = m_v T_a\, (s_{3'} – s_3)$ **(SPP.4)**

It is represented by tyhe green area in Figure 11.

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[13] In reality, friction losses are distributed along the pipes of the economizer, evaporator and superheater; mosto f them are concentrated in this last as the specific volume of the fluidi s larger; so this is a reasonable approximation.

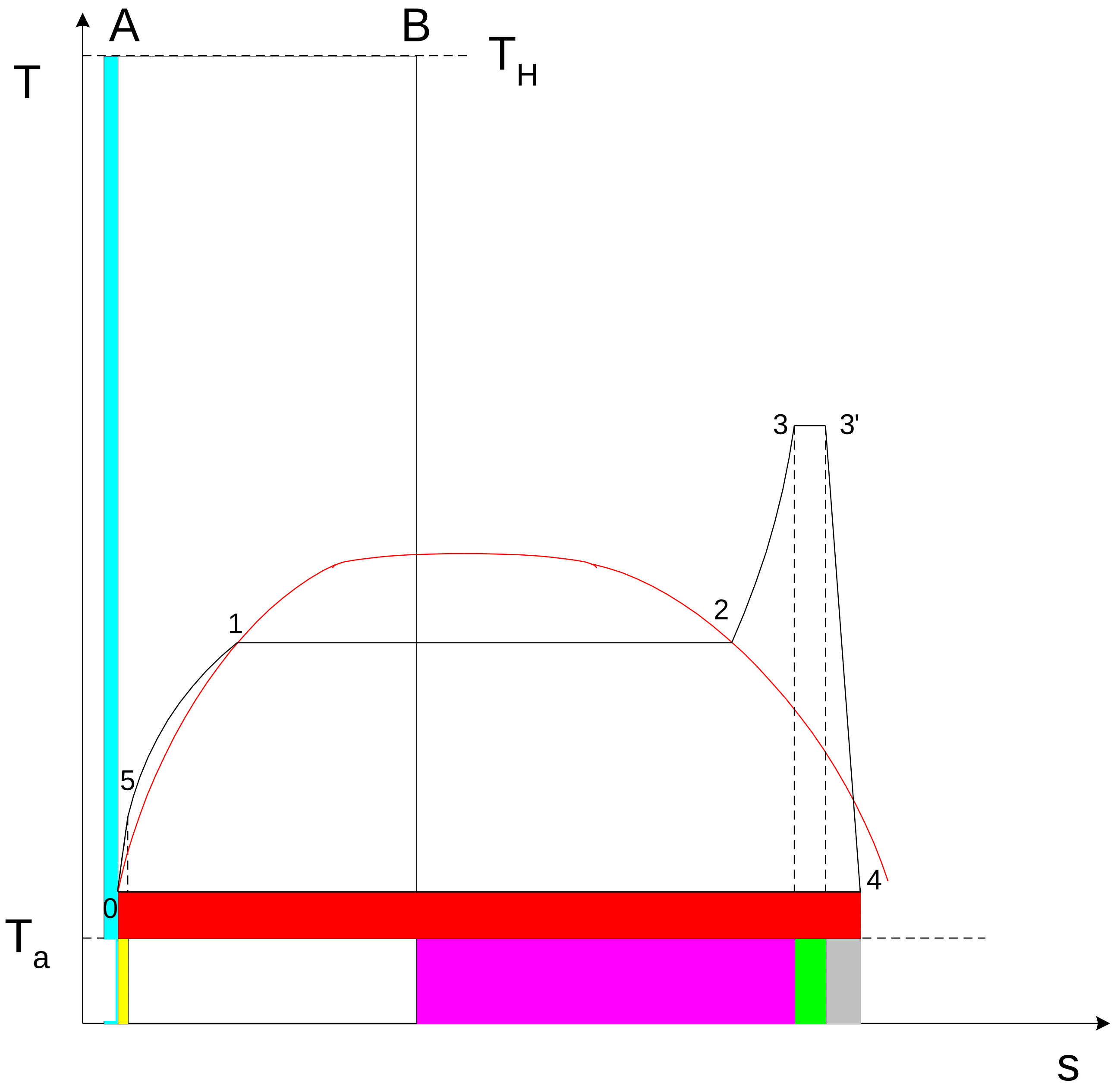

Figure 11 – Exergy destruction and losses for steam power plant

<u>Turbine exergy destruction</u>

Again, this is given (adiabatic transformation) by $T_a \Delta S_{irr}$*, with* ΔS_{irr} *typically calculated knowing the turbine isentropic efficiency:*

$$E_{DT} = T_a\,(S_4 - S_{3'}) = m_v T_a\,(s_4 - s_{3'}) \qquad \text{(SPP.4)}$$

The turbine exergy destruction is graphucally represented by the grey area in Figure 11..

Condenser exergy loss

Globally, it is represented by the loss of all the exergy of the transformation within the condenser, from nearly saturated steam to saturated liquid:

$$E_{LC} = m_v\,[(h_4 - h_0) - T_a\,(s_4 - s_0)] \qquad \text{(SPP.5)}$$

The condenser exergy loss is represented by the red box shown in Figure 11, lying over T_a and having a height (T_4 -T_a) and base (s_4 –s_0).

For a more detailed analysis, the condenser can be treated as a component with a heat transfer exergy destruction (heat transferred between condensing steam and the external coolant stream) and an exergy loss (released of the warm coolant to the environment). The sum of these contributions is the same as for the global approach.

Pump exergy destruction

As for the turbine, the pump exergy destruction can be expressed as $T_a\Delta S_{irr}$, with ΔS_{irr}typically calculated knowing the pump isentropic efficiency:

$$E_{DP} = T_a\,(S_5 - S_0) = m_v T_a\,(s_5 - s_0) \qquad \text{(SPP.6)}$$

The pump exergy destruction is represented by the yellow area in Figure 11.

Please notice from Figure 11 that all exergy losses appearas rectangles above T_a; all exergy destructions are represented by rectangular boxes having heigth T_a..

Reminder – Entropy of perfect gases (and liquids)

The following is a reminder of the expression of entropy for perfect gases, which is necessary in the following in order to focus the analysis on reactive systems.
In general, entropy as a state function is defined as $ds = dQ/T$; then, we can refer to a perfect gas operating in an open system (a similar approach can be followed for closed systems).

$$du = dQ + dW = Tds - pdv$$

$$d(pv) = pdv + vdp \qquad\qquad p\,dv = d(pv) - v\,dp$$

$$Tds = du + pdv = d(u + pv) - vdp = dh - vdp$$

$$ds = dh/T - (v/T)dp \qquad\qquad (v/T) = R/p$$

$$ds = c_p dT/T - Rdp/p$$

Assuming the Reference State (T_a=298.15 K; p_a=101325 Pa):

$$s - s_a = c_p \ln(T/T_a) - R \ln(p/p_a) \qquad (28)$$

Eq. 28 allows to evaluate the entropy of a perfect gas knowing two physical variables (pressure and temperature; two variables are needed for a perfect gas, $s = f(p, T)$).

It is worth to recall that for a liquid in an open system $dp = 0$ under reversible conditions, which implies the absence of work, so that $dQ = dh = Tds$; adding that $dh = c\,dT$, it results that:

$$s - s_a = c \ln(T/T_a) \qquad (29)$$

that is, entropy of a liquid is only a function of temperature (not of pressure).

Entropy of mixing (real, irreversible processes)

As happens for pressure, volume, mass, internal energy and enthalpy, also entropy can be treated with the general approach in the case of mixture: that is, for all these state function the additive property can be applied (the mixture property results from the sum of the properties evaluated for all the separate components of the mixture)[14].

Perfect gas mixtures are particularly relevant because they represent combustion products with very good accuracy. The same holds for air (mixture of nitrogen, oxygen and water vapor).

Dealing with entropy for a mixture of perfect gases, for each component $s_i=f(p_i,T_i)$; applying the additive property, one gets

$S = \Sigma_i S_i$.

This does not mean that true mixing processes are isentropic. In fact, mixing gives rise to large irreversibilities. In order to achieve a reversibile mixing, each component should enter the control volume with a partial pressure equal to that in the already formed mixture. Such a process would be exceedingly slow (consequently, reversible), because uniformation of the component inside the mixture would be obtained only by diffusion (Fick's law; molecular diffusion). Of course, also temperature should be homogeneous. In practice, isothermal mixing conditions can be recommended, but it is impossible to supply the single components at the exact partial pressure value; rather (considering for example atmospheric combustion processes), the components (e.g., natural gas and air) are both supplied at ambient pressure (which is also the resulting mixture pressure, with reactants exiting at combustor outlet – still with no flame).

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[14] This applies only for non-reactive systems, that is, to systems where the mixture components do not establish chemical bonds among the different species. In such cases, energy and entropy contributions linked to the establishment of the bond arise.

As an example, consider natural gas supplied (*from the utility gas network*) at a pressure slightly higher than ambient; air is drawn by a fan - always at a pressure close to the atmospheric value.

Consequently, each mixture component undergoes a throttling process from its original supply pressure (close to atmospheric) to its partial pressure within the mixture (whose overall pressure is atmospheric; that is, the components partial pressures are smaller).[15] This throttling process is irreversible and can be large for practical applications (such as mixing of the reactants for a combustion system). Referring to an isothermal process and to perfect gases, the mixing exergy destruction can be computed as:

$$L_{mix} = T_a \Delta S_{mix} = T_a R_M \Sigma_i \nu_i \ln (p/p_i) \qquad \text{[W] (30)}$$

In Eq. 30, ν_i is the number of moles per second of species i,

$\nu_i = {}^{\dot{m}_i}/_{M_i}$. ($M_i$ = molecular mass of species i; R_M = universal gas constant J/(kmol K)). For engineering purposes Eq. 22 can be rearranged referring to the overall mass flow rate $\dot{m}$:

$$L_{mix} = \dot{m} T_a R_m \Sigma_i M_i x_i \ln (p/p_i) \qquad \text{[W] (30')}$$

R_m is the mixture gas constant [J/(kg K)], and $x_i$is the volumetric (or molar) concentration of species i inside the mixture.

---

[15] Indeed, from the point of view of thermodynamics it is possible to postulate the existence of special devices, named Van't Hoff boxes, allowing selective recovery of this throttling work; in practice a Van't Hoff box is a special reversible turbine operating on one single species within a mixture. Such devices do not exist in reality. For more details see R. A. Haywood, Equilibrium thermodynamics for engineers and scientists, Wiley, 1980.

Reactive Systems (Combustion). Generalities.

In general, combustion reactants are supplied to the combustor under non-isothermal conditions and with pressures different from the partial pressures within the homogeneous mixture.

A combustion process can be split in three steps to put in evidence the chemical irreversibility in strict terms:

1) providingThermal equilibrium of the reactants, reaching homogeneous temperature conditions (1→1’; 2→2’). Ideally, this should take place recovering heat reversibly (using heat exchangers with no local temperature difference)
2) providing Mechanical equilibrium of the reactants, adapting their pressure to the partial pressure required in the perfectly-mixed reactants. (1’→1”; 2’→2”). This could ideally be done reversibly introducing an expander with unitary isentropic efficiency, working between the supply pressure and the partial pressure of the species inside the mixture[16].
3) Chemical reaction between the perfectly mixed reactants, resulting in the Products of combustion (1”+2” → 3)

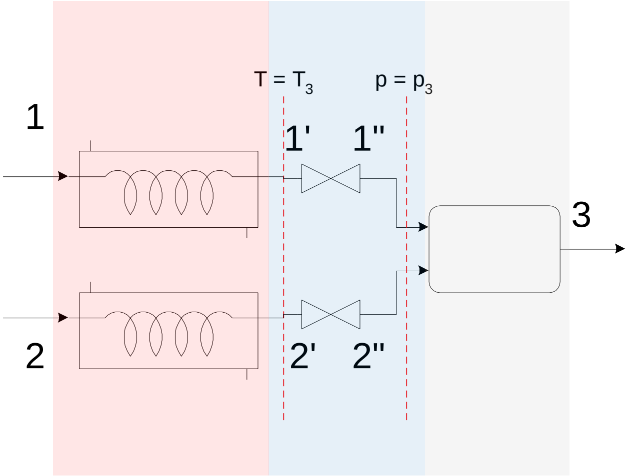

Figure 12 - Scheme of a three-stage combustion process (Temperature equilibrium + Mechanical equilibrium= Mixing +**Chemical reaction**)

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[16] That is, the Van’t Hoff box described before in note 15.

It should be underlined that in some relevant cases, instead of recovering expansion work it can be necessary to provide compression work, so that a reactant stream is able to enter the reaction chamber volume where the overall pressure is 1 bar; for example, this is true for Oxygen, normally drawn from the atmospheric environment at a standard pressure of 21000 Pa; this means that compression is needed to reach the partial pressure required for atmospheric (mixture) pressure combustion. This compression work can be supplied by a fan, or derived from combustion-related energy transfer (e.g., common flames with entrained combustion air).

Combustion Systems. Energy analysis (Thermochemistry)

Combustion reactions are often used as they are able to release important Energy rates, usually made available as high-temperature heat. The number of complete combustion reactions is very limited when considering the original elements (C, H, S):

$$C + O_2 = CO_2 + \Delta H_{ofCO2} \qquad \Delta H_{ofCO2} = -394.MJ/kmol \qquad (31)$$

$$H_2 + ½\, O_2 = H_2O + \Delta H_{ofH2O} \qquad \Delta H_{ofH2O} = -242\ MJ/kmol \qquad (32)$$

$$S + O_2 = SO_2 + \Delta H_{ofSO2} \qquad \Delta H_{ofSO2} = -298\ MJ/kmol \qquad (33)$$

As the reactants are elements (present in the reference environment), these are called Formation Reactions. For each reaction, the value of the *Standard Heat of Formation* in the reference conditions (25°C = 298,16K) is given. This is a negative value (heat exiting the exothermic reaction). The values of ΔH_{of} are not many, and they are available – also tabulated as a function of temperature - since a long time for all species of technical interest[17].

ΔH_{of} is defined as the heat which is produced as a result of the ideal reaction where 1 kmol of products is formed starting from the corresponding elements at the standard temperature of 298.16 K and pressure 1 bar. It can also be defined as the variation of enthalpy from reactants (elements) to products in standard conditions.

Thermochemical practice assumes that moles of reactants (entering) are negative, and products (exiting) are positive; as the heats of formation are negative, this is compliant with the assumptions done for heat and work flows; on the product side, a negative ΔH_{of} represents a useful output of the system (reaction).

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[17] JANAF, NASA Tables

Hess Law – The Additive property in thermochemistry

The Hess law affirms the additive property for general chemical reactions. In the following example, it is shown for two reactants (not necessarily elements) and two products:

$$\nu_a A + \nu_b B \leftrightarrow \nu_c C + \nu_d D \tag{34}$$

The Hess law states that the enthalpy variation between reactants A and B and products C and D can be calculated by the simple sum:

$$\Delta H^0 = \nu_c \Delta H_f^0(C) + \nu_d \Delta H_f^0(D) - \nu_a \Delta H_f^0(A) - \nu_b \Delta H_f^0(B) \tag{35}$$

Where ν_i is the number of moles of species i. A useful consequence of Eq. 35 is that from the knowledge of the *Heats of Formation* ΔH_f^o, it is possible to derive the *Heats of Reaction* ΔH^o for any chemical reaction of technical interest. This represents a great simplification, because it limits the necessary data to those tabulated in standard collections of ΔH_f^o (Janaf, NASA,…). Eq. 35 can be generalized as:

$$\Delta H_r^0 = \sum_k \nu_k \Delta H_{f_k}^0 = \left(\sum_j \nu''_j \Delta H_{f_j}^0 \right)_P - \left(\sum_i \nu'_i \Delta H_{f_i}^0 \right)_R \tag{36}$$

Where v''_j is the number of moles of the j-th productand v'_I the number of moles of the i-th reactant.

The Heat of Reaction is closely linked to the Lower Calorific Value in standard conditions:

$$H_{ci} = -\frac{\Delta H_r^o}{M_f} \tag{37}$$

Where M_f is the molecular mass of the fuel. We are referring to the Lower Calorific Value because all the products (including water vapor) are assumed to be in gaseous state.

The **standard state** for elements is referred to the state of aggregation at the standard values of temperature and pressure. Referring to other substances (compounds), gases are substances which behave approximately as perfect gases at standard conditions; the same holds for liquids and solids. For water, the reference conditions are referred to the atmospheric environment (water vapor in wet air at reference conditions)[18].

Elements can be found in the reference environment; consequently, their Standard Heat of Formation is zero by definition ($\Delta H_f^o = 0$).

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[18] This is a relevant difference with respect to the standard steam property tables, which assume zero enthalpy and entropy at 1 bar and 0°C. In terms of energy, the difference is large as it includes the heat of phase transition.

Extension of Exergy to reactive systems (1)

Dealing mainly with combustion reactions, most of which taking place at atmospheric or moderate pressure, reactants and products can be assimilated to perfect gas mixtures, for which[19]:

$$dh = c_p\, dT \qquad (38)$$

$$ds = c_p\, dT/T - R(dp/p) \qquad (39)$$

that is, performing an indefinite integral:

$$h = c_p T + A \qquad (40)$$

$$h - h_a = c_p\, (T - T_a) \qquad (40')$$

$$s = c_p \ln T - R \ln p + B \qquad (41)$$

$$s - s_a = c_p \ln (T/T_a) + R \ln(p/p_a) \qquad (41')$$

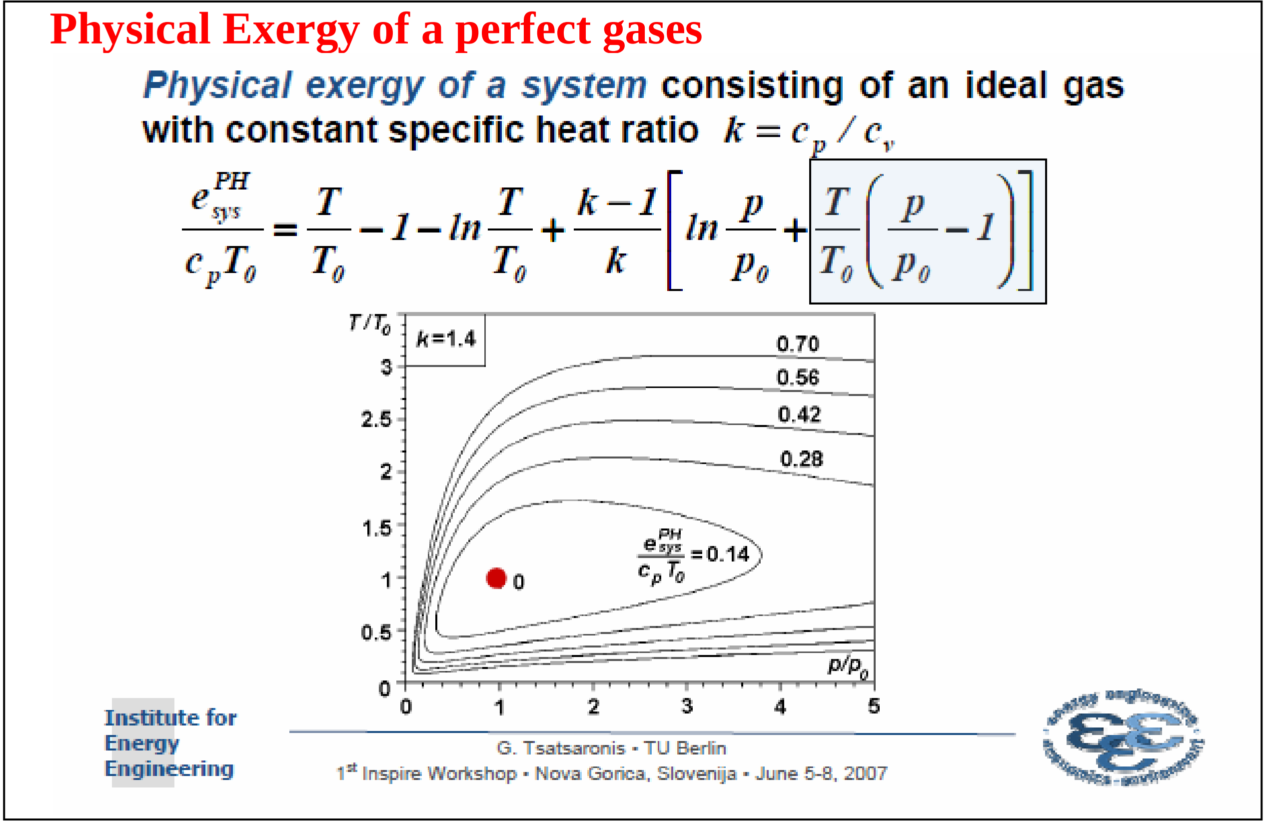
where constants A e B depend on the reference state (as is shown by the definite integral form ‘).

---

[19] Indeed air or natural gas (in the reactants) behave as perfect gases; in the combustion products, the main species CO2 and H2O are present at partial pressures well below the critical value for the specific species, so that perfect gas behavior results to be a realistic hypothesis. When considering **liquid or solid fuels**, the volume occupied by the fuel is very small so that it does not change the perfect gas behavior of the reacting air (so these can be treated as limit cases, assuming that the volume of the fuel fraction is zero). Of course there are exceptions: for example, when advanced combustion power cycles are considered (Matiant, Allam) working with Oxygen as oxidizer, pressures are pushed to high values in order to have compact units with high power and facilitate pressurized CO2 sequestration. In these extreme cases, CO2 and H2O can be treated as a mixture of real fluids (not perfect gases), eventually considering also solubility of CO2 in liquid water in the low-temperature section of the semi-closed cycle.

At this point, the specific exergy of a perfect gas can be calculated as:

$$e = (h-h_a) - T_a\,(s-s_a) = c_p\,(T- T_a) - T_a\,c_p \ln (T/T_a) + T_a R \ln (p/p_a) \qquad (42)$$



Physical Exergy of a perfect gases

Physical exergy of a system consisting of an ideal gas with constant specific heat ratio $k = c_p / c_v$

$$\frac{e^{PH}_{sys}}{c_p T_0} = \frac{T}{T_0} - 1 - \ln\frac{T}{T_0} + \frac{k-1}{k}\left[\ln\frac{p}{p_0} + \boxed{\frac{T}{T_0}\left(\frac{p}{p_0} - 1\right)}\right]$$

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The *Gibbs Free Energy* is defined as g = h – Ts; for a perfect gas:

$$g = h - Ts = c_p T(1 - \ln T) + RT \ln p - BT + A \qquad (43)$$

Referring to moles:

$$g_M = \phi_M + R_M T \ln p \qquad (44)$$

with the term ϕ_M only function of temperature:

$$\phi_M = c_{pM}\, T\,(1 - \ln T) - B_M T + A_M \qquad (45)$$

Chemical Exergy (1)

When the reference conditions (p_a, T_a) are reached, corresponding to thermo-mechanical equilibrium with the reference environment, Physical Exergy $x = (h-h_a) - T_a (s-s_a) = 0$ by definition ($h=h_a$, $s=s_a$). Any possibility of extracting work from the system under these conditions is linked with a variation of the Gibbs free Energy g = h - T s, obtainable through a chemical transformation from reactants to products.

The variation of Gibbs Free Energy in the transformation, taking place at T_a, p_a, is:

$$\Delta G_{Mo} = \Sigma_k \nu_k \Delta G_{fok} = \Sigma_k \nu_k \mu_{ko} \qquad (46)$$

Where the standard chemical potentials referred to 1 kmol are introduced, $\boldsymbol{\mu_{k_0} = \Delta G_{fok}}$; conceptually, these are referred to a reaction of formation from the elements. $\mu_{k_0} = \Delta G_{fok}$ represents the maximum (reversible) possibility of obtaining work producing 1 kmol of product k from the necessary elements at standard reference conditions.

If the molar Standard Free Energy of formation is not available, one can calculate it from repertories of ΔH_f^o and Δs_f^o; then, as was done for Hess law, one can apply the additive property so that, for a general reaction from reactants to products, the variation of the Free Energy of Reaction is:

$$\Delta G_M^o = \Delta H_M^o - T_a \Delta s_M^o = \sum_k \Delta H_{fk}^o - T_a \sum_k \Delta s_{fk}^o \qquad (47)$$

Example: Stoichiometric combustion of Methane in an Oxygen stream

Reaction: $CH_4 + 2\ O_2 \Leftrightarrow\ CO_2 + 2\ H_2O$

For the calculation of ΔG_{Mo} *(1 kmol di CH4 at 1 bar, 298,15 K):*

$$\Delta G_{M}0 = 1\cdot(\Delta G_{f0})_{CO2} + 2\cdot(\Delta G_{f0})_{H2O} - 1\cdot(\Delta G_{f0})_{CH4} =$$

$$= -394.35 \quad -2 * 228.7 \quad -(-50.8) \ = -800903\ kJ/kmol$$

Please notice that both reactants and products are at standard (atmospheric pressure). Referring to the products (3 kmoles), this means that the partial pressure of water vapor H2O is 0,66 bar; the partial pressure of CO2 in the products is 0,33 bar. These values are obviously not in chemical equilibrium with the environment.

Extension of Exergy to reactive systems (2)

Equations 46 and 47 state that, at the Reference state thermodynamic conditions (p_a, T_a; zero physical exergy), the only contributions to exergy can be of chemical nature; that is, chemical exergy - which is given by the product of number of moles and the chemical potential (or Molar Free Energy of Formation) of each species considered.(positive sign for products, negative for reactants).

Consequently, the knowledge of the difference ΔG_{mo} for the reaction leading from reactants to products, calculated as $\Sigma_k \nu_k \Delta G_{fok}$, allows to evaluate the maximum (reversible) work obtainable from a chemical reaction taking place at standard conditions. The molar values of the Free Energy of Formation $\Delta G_{fok} = \mu_{ko}$ at standard conditions are available for all the fundamental chemical compounds. This allows to generalize the **open-system steady-flow availability for reactive flows**:

$$b = h - T_a s - \Sigma_k \nu_k \mu_{ko} \quad (48)$$

As usual, Exergy (inclusing now physical and chemical exergy) is given by the difference between availability at the state under exam and that of the standard reference environment, $x = b - b_a$.

Chemical Exergy (2). Reference state.

From the point of view of Physical Exergy, it is sufficient to define the reference environment in terms of pressure and temperature (thermo-mechanical restricted equilibrium). **Unrestricted Equilibrium** is reached when the system reaches also the same chemical composition of the reference environment; this is also called the **Dead State**, as at this stage there is no possibility of obtaining useful work through interaction of the system with the environment.

When calculating chemical exergy, reference was made to a reaction taking place at the reference conditions, p_a, T_a. However, nothing was said about interaction of the products with the reference environment; in the example related to stoichiometric combustion of Methane, however, it was anticipated that the combustion products were clearly not in chemical equilibrium with the environment. This means that a further correction is needed to account for interaction of the products with the reference environment.

Indeed **Chemical Exergy** can be formally defined as the maximum work obtainable when a substance is taken from the reference state p_a, T_a to the dead state (unrestricted equilibrium with the environment); this can be obtained through processes of heat and mass transfer. In other words chemical exergy represents the exergy of a stream matter when it is at ambient pressure and temperature.

As we are ideally operating in a reversible world, chemical exergy can be defined starting from the dead state: in these terms, it results to be the minimum amount of work needed to synthesize a substance from the reference environment (a process which can be activated through the use of heat and mass transfer only).

Consequently, it is very important to define in precise terms the **reference environment** in order to perform calculations of chemical exergy.

The reference environment should contain all fundamental species necessary to synthesize any substance; moreover, it should be built giving priority to commonly available substances.

The reference environment considers substances available in the atmosphere, in the oceans and in the earth crust. This fundamental work was set by the Polish scientific school (Prof. Jan Szargut[20]) and the most common repository for updated data can be found in the Exergoecology Portal[21].

---

[20] Szargut, J., Morris, DR, Steward, FR, Exergy Analysis of Thermal, Chemical and Metallurgical Processes, Hemisphere, 1988.

[21] http://www.exergoecology.com/excalc

Table 1: Gaseous reference environment – Partial pressure and standard chemical exergy of various gaseous substances at 298.15 K e 101325 Pa (Szargut, et al., 1988).

Reference species					
Element	Substance	Molar fraction in dry air	Conventional partial pressure [kPa]	Substance Standard chemical exergy [kJ/kmol]	Element Standard chemical exergy [kJ/kmol]
Ar	**Ar**	**0.009 33**	**0.906**	**11.69**	**11.69**
C grafite	**CO_2**	**0.000 345**	**0.0335**	**19.87**	**410.26**
D_2	**$D_2O_{(g)}$**	**0**	**0.000 342**	**31.23**	**263.79**
H_2	**$H_2O_{(g)}$**	**0**	**2.2**	**9.49**	**236.09**
He	**He**	**0.000 005**	**0.000 485**	**30.37**	**30.37**
Kr	**Kr**	**0.000 001**	**0.000 097**	**34.36**	**34.36**
N_2	**N_2**	**0.7803**	**75.78**	**0.72**	**0.72**
Ne	**Ne**	**0.000 018**	**0.001 77**	**27.19**	**27.19**
O_2	**O_2**	**0.2099**	**20.39**	**3.97**	**3.97**
Xe	**Xe**	**0.000 000 09**	**0.000 008 7**	**40.33**	**40.33**

Table 2: Average concentration and standard chemical exergy of substances in the marine environment (ocean water) (Szargut, et al., 1988).

	Reference species			
Element	Substance	Molarity [kmol/kgH_2O]	Activity Coefficient	Element standard chemical exergy [kJ/kmol]
Ag(s)	$AgCl_2^-$	$2.7*10^{-9}$	0.6	70.2
As(s)	$HAsO_4^{2-}$	$2.1*10^{-8}$	0.1	494.6
Au(s)	$AuCl_2^-$	$5.8*10^{-11}$	0.6	15.4
B(s)	$B(OH)_3$	$3.4*10^{-4}$	1.0	628.5
Ba(s)	Ba^{2+}	$1.4*10^{-7}$	0.2	747.7
Bi(s)	BiO^+	$1*10^{-10}$	0.6	274.5
Br_2(l)	Br^-	$8.7*10^{-4}$	0.68	101.2
Ca(s)	Ca^{2+}	$9.6*10^{-3}$	0.21	712.4
Cd(s)	$CdCl_2$	$6.9*10^{-11}$	1.0	293.8
Cl_2(g)	**Cl^-**	**0.5657**	**0.68**	**123.6**
Co(s)	Co^{2+}	$6.8*10^{-9}$	0.2	248.6
Cs(s)	Cs^+	$2.3*10^{-9}$	0.6	404.4
Cu(s)	Cu^{2+}	$7.3*10^{-10}$	0.2	134.2
F_2(g)	F^-	$3.87*10^{-5}$	0.68	466.3
Hg(l)	$HgCl_4^{2-}$	$3.4*10^{-10}$	0.1	115.9
I_2(s)	IO_3^-	$5.2*10^{-7}$	0.6	174.7
K(s)	*K^+*	*$1.04*10^{-2}$*	*0.64*	*366.6*
Li(s)	Li^+	$2.5*10^{-5}$	0.68	393.0
Mg(s)	*Mg^{2+}*	*$4.96*10^{-2}$*	*0.23*	*611.0*
Mn(s)	Mn^{2+}	$7.5*10^{-9}$	0.2	422.0
Mo(s)	MoO_4^{2-}	$1.1*10^{-7}$	0.1	730.3
Na(s)	**Na^+**	**0.474**	**0.68**	**336.6**
Ni(s)	Ni^{2+}	$1.2*10^{-7}$	0.2	232.7
P(s)	HPO_4^{2-}	$4.9*10^{-7}$	0.1	861.4
Pb(s)	$PbCl_2$	$4.2*10^{-11}$	1.0	232.8
Rb(s)	Rb^+	$1.42*10^{-6}$	0.6	388.6
S(s)	*SO_4^{2-}*	*$1.17*10^{-2}$*	*0.11*	*609.6*
Se(s)	SeO_4^{2-}	$1.2*10^{-9}$	0.1	346.5
Sr(s)	Sr^{2+}	$8.7*10^{-5}$	0.2	730.2
W(s)	WO_4^{2-}	$5.6*10^{-10}$	0.1	827.5
Zn(s)	Zn^{2+}	$1.7*10^{-8}$	0.2	339.2

Bold : contributions> 10^{-1} *Red Contributions > 10^{-2}*

Table 3: Average concentrationsand standard chemical exergy of reference species in the earth crust (Szargut, et al., 1988).

			Reference species			
Element	Subst. in earth crust	Mass fraction	Formula	Molar fraction	Substance chemical exergy [kJ/kmol]	Element chemical exergy [kJ/kmol]
Al	**Al_2O_3**	**0.152**	**Al_2SiO_5**	**$2*10^{-3}$**	**15.4**	**888.4**
Ba	BaO	$5.1*10^{-3}$				
Ca	CaO	$5.1*10^{-2}$				
Cl_2	Cl	$4.5*10^{-4}$				
Co(s)	Co	$4*10^{-5}$	Co_3O_4	$2*10^{-7}$	38.2	265.0
Cr(s)	Cr_2O_3	$5.2*10^{-4}$	Cr_2O_3	$4*10^{-7}$	36.5	544.3
Fe(s)	FeO	$3.72*10^{-2}$				
	Fe_2O_3	$3.10*10^{-2}$	Fe_2O_3	$1.3*10^{-3}$	16.5	376.4
K	K_2O	$3.11*10^{-2}$				
Mg(s)	MgO	$3.45*10^{-2}$	$MgCO_3$	$2.3*10^{-3}$	15.1	633.8
Mn(s)	MnO	$1.18*10^{-3}$	MnO_2	$2*10^{-4}$	21.1	482.3
Na	Na_2O	$3.71*10^{-2}$				
P(s)	P_2O_5	$2.85*10^{-3}$	$Ca_3(PO_4)_2$	$4*10^{-4}$	19.4	875.8
S	SO_3	$2.6*10^{-4}$				
Sb(s)	Sb	$1*10^{-6}$	Sb_2O_5	$7*10^{-10}$	52.3	435.8
Si(s)	**SiO_2**	**0.591**	**SiO_2**	**0.472**	**1.9**	**854.6**
Sn(s)	Sn	$4*10^{-5}$	SnO_2	$8*10^{-6}$	29.1	544.8
Ti(s)	TiO_2	$1.03*10^{-2}$	TiO_2	$1.8*10^{-4}$	21.4	906.9
U(s)	U	$4*10^{-6}$	UO_3	$2*10^{-8}$	43.9	1190.7
V(s)	V_2O_5	$2.3*10^{-4}$	V_2O_5	$2*10^{-6}$	32.5	712.1

Bold: mass contribution> 10^{-1}Red: mass contribution > 10^{-2}

Interaction of products with the reference environment

The Reference State is now defined also in terms of chemical composition. Conceptually, it is still possible to obtain useful work from the reaction products (p_a= 101,325kPa; T_a= 25°C) through an interaction with the environment; to do this, one should hypothesize a transformation from the condition of release of the products to the concentration levels of the same species in the reference environment.

As an example, if the following equation is taking place at standard conditions:

$$CH_4 + 2\ O_2 = CO_2 + 2\ H_2O \qquad (49)^{22}$$

The partial pressures of the species involved are:

Products p_{CO2} = 33437kPa; p_{H2O} = 66875 kPa

Ractants p_{CH4} = 33437kPa; p_{O2} = 66875 kPa

CH_4 is available at the network pressure (slightly above 101,325 kPa for urban district final user gas networks; 3-7 MPa for large users directly connected to the gas pipeline[23]) and there is a tradition of recovering at least partially the expansion work.

---

[22] Notice that all the following considerations remain valid also when combustion in air is considered; in fact, in this case for each kmole of O2 there are about 79/21 kmoles of N2 which appear both as reactants and products; this is consequently only a dilution term and does not change the compression or expansion works discussed below.

[23] The technical problem is with gas cooling during expansion, which can cause precipitation of solid hydrates which are dangerous for the seals. In any case, pressure recovery is performed down to atmospheric pressure – never below that; while the partial pressures of the products or reactants should ideally be considered.

Instead, it is important to focus on “hidden” contributions from reactants and products:

a) Oxygen is present in the reference environment at a partial pressure of 20,39 kPa; in order to participate to the combustion reaction, it needs to be compressed to 66,9 kPa;

b) CO2 and H2O have partial pressures in the products which are well above to those in the reference environment (respectively 0,0335 kPa and 2,2 kPa); consequently, it would be possible to activate a selective expansion process[24] from the partial pressure in the products to that in the reference environment. This expansion work is actually lost when the combustion products are released to the environment under non-equilibrium (chemical) conditions.

Consequently, rather than considering the combustion irreversibility only in terms of ΔG_{M0} neglecting the discharge of products in the environment under non-(chemical)-equilibrium conditions[25], it is necessary to add a specific term accounting for chemical interaction of combustion products (and reactant O2) with the environment[26].

---

[24] This would require a specific Van’t Hoff box (Notes 15-16), composed of a reversible semi-permeable membrane allowing only the specific species to permeate without any throttle pressure loss; followed by a reversible expander.

[25] This is actually the approach followed in the reference book of thermodynamics, E. P. Gyftopoulos; G. P. Beretta, *Thermodynamics: Foundations and Applications*, Mineola (New York), Dover Publications, 2005

[26] The correction term is largest for highly-hydrogenated fuels, such as methane; in this case, it represents about 5% of ΔG_{M0}

The corrective term can be calculated considering that the combustion products behave as a perfect gas mixture, hypothesizing an isothermal expansion process from the partial pressure in the products to that of the species in the reference environment.

If the species k is in thermomechanical equilibrium conditions (101,325 kPa; 298,15 K), the expansion work for 1 kmol of pure substance would be given by:

$$\tilde{\varepsilon}_{0k} = \tilde{R}T_a ln \frac{p_a}{p_{a0i}} \qquad (50)$$

Where p_{a0i} is the partial pressure of species i in the reference environemnt (Table 1).

In reality, the combustion products are at ambient pressure from the point of view of the mixtture, but each species has a partial pressure which is lower than that. Consequently, we should consider each species at its individual partial pressure in the products, and include the compression term for oxygen. As a consequence, the Chemical Exergy of a fuel is finally given by:

$$\tilde{\varepsilon}_0 = -\Delta\tilde{h}_0 + T_a \Delta\tilde{s}_0 + \tilde{R}T_a \left(x_{O_2} \ln \frac{p_{a0O_2}}{p_a} - \sum_i x_i \ln \frac{p_{a0i}}{p_a} \right) \qquad (51)$$

Example – Combustion of CH_4 (Flametgpm1.ees)

The software EES[27] allows to calculate ΔG_{fok} fro the ΔH_{fok}, and Δs_{fok}:

$h_{ch40} = \mathbf{h}('CH4'; T=t0)$ $\quad h_{o20} = \mathbf{h}('O2'; T=t0)$

$h_{n20} = \mathbf{h}('N2'; T=t0)$ $\quad s_{ch40} = \mathbf{s}('CH4'; T=t0; P=p0)$

$s_{o20} = \mathbf{s}('O2'; T=t0; P=p0)$

$s_{n20} = \mathbf{s}('N2'; T=t0; P=p0)$ $\quad h_{cO20} = \mathbf{h}('CO2'; T=t0)$

$h_{H2O0} = \mathbf{h}('H2O'; T=t0)$

$s_{cO20} = \mathbf{s}('CO2'; T=t0; P=p0)$

$s_{H2O0} = \mathbf{s}('H2O'; T=t0; P=p0)$

$DG_{ch4} = h_{ch40} - t0 \cdot s_{ch40}$

$DG_{O2} = h_{o20} - t0 \cdot s_{o20}$ $\quad DG_{N2} = h_{n20} - t0 \cdot s_{n20}$

$DG_{CO2} = h_{cO20} - t0 \cdot s_{cO20}$

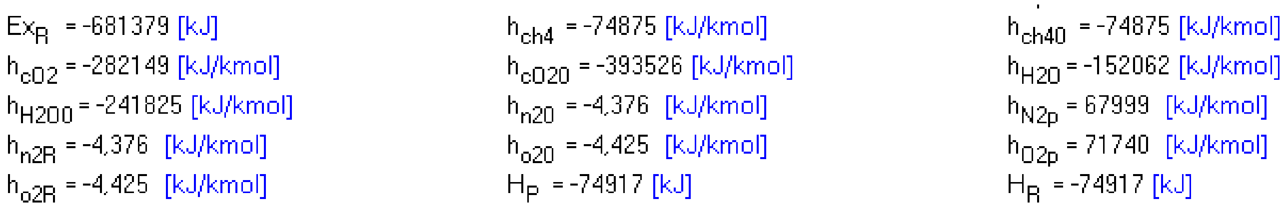
$DG_{H2O} = h_{H2O0} - t0 \cdot s_{H2O0}$

Reaction:
CH4 + 2 (1+X/100) (O2 + 3.76 N2)

<--> CO2 + 2 H2O + 3.76 (2 + 2 X/100) N2 + 2X/100 O2

T is the adiabatic combustion temperature, assuming no dissociation. X is the % excess air.

Solution(Enthalpies)[28]:



$Ex_R = -681379$ [kJ] $\quad h_{ch4} = -74875$ [kJ/kmol] $\quad h_{ch40} = -74875$ [kJ/kmol]

$h_{cO2} = -282149$ [kJ/kmol] $\quad h_{cO20} = -393526$ [kJ/kmol] $\quad h_{H2O} = -152062$ [kJ/kmol]

$h_{H2O0} = -241825$ [kJ/kmol] $\quad h_{n20} = -4,376$ [kJ/kmol] $\quad h_{N2p} = 67999$ [kJ/kmol]

$h_{n2R} = -4,376$ [kJ/kmol] $\quad h_{o20} = -4,425$ [kJ/kmol] $\quad h_{O2p} = 71740$ [kJ/kmol]

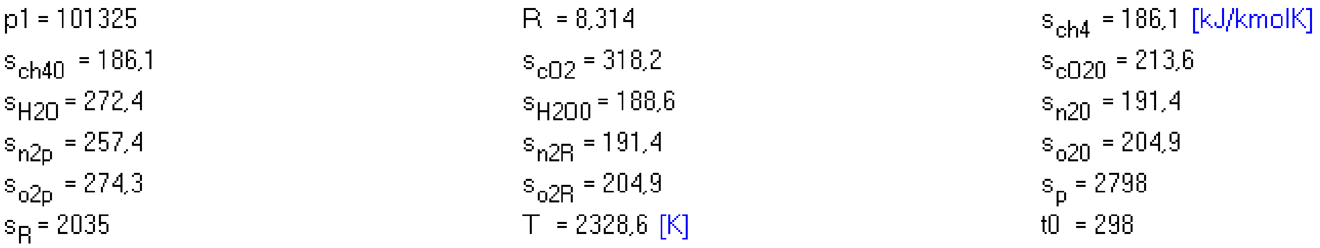
$h_{o2R} = -4,425$ [kJ/kmol] $\quad H_P = -74917$ [kJ] $\quad H_R = -74917$ [kJ]

---

[27] EES call to substances with chemical formulas imply perfect gas assumption

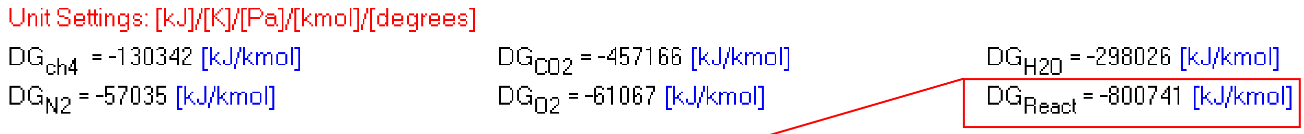
[28] The reference state in EES is different from the JANAF tables.

Solution (Entropies):



```
p1 = 101325            R  = 8,314             sch4  = 186,1 [kJ/kmolK]
sch40  = 186,1         sc02 = 318,2           sc020 = 213,6
sH20 = 272,4           sH200 = 188,6          sn20  = 191,4
sn2p  = 257,4          sn2R  = 191,4          so20  = 204,9
so2p  = 274,3          so2R  = 204,9          sp = 2798
sR = 2035              T  = 2328,6 [K]        t0  = 298
```

Solution[29] ΔG_{fok}*:*



```
Unit Settings: [kJ]/[K]/[Pa]/[kmol]/[degrees]
DGch4  = -130342 [kJ/kmol]      DGCO2 = -457166 [kJ/kmol]      DGH2O = -298026 [kJ/kmol]
DGN2 = -57035 [kJ/kmol]         DGO2 = -61067 [kJ/kmol]        DGReact = -800741 [kJ/kmol]
```

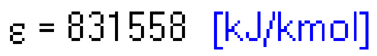
Equatione for reaction ΔG_o*:*

$$DG\_React = -1*DG\_ch4 \quad - 2*(1+X/100)*DG\_O2$$
$$- 2*(1+X/100)*3{,}76*DG\_N2 + \quad DG\_CO2 + \quad 2*DG\_H2O$$
$$+ 2*(1+X/100)*3{,}76*DG\_N2 + 2*X/100*DG\_O2$$

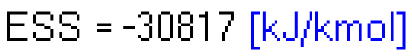
Interaction with the reference environment:

$$ESS = -R*T_a*(\underbrace{2*\ln(0{,}2039/1{,}01325)}_{\text{O2 (2 kmoles in ractants)}} - \underbrace{\ln(0{,}000345/1{,}01325)}_{\text{CO2 (1 kmolesin products)}} \underbrace{-2*\ln(2{,}2/101{,}325)}_{\text{H2O (2 kmoles in products)}})$$

Chemical exergy of CH4: $\quad Epsilon = -(DG\_React + ESS)$



```
ε = 831558  [kJ/kmol]
```



```
ESS = -30817 [kJ/kmol]
```

Please notice (inside the program)that energy is conserved between Reactants and Products ($H_P = H_R$*; allowing the calculation of the flame adiabatic temperature, if this is not explicitly given). However,* $S_P > S_R$*, which allows to calculatethe* ***Combustion Exergy Destruction*** *as* $EXD_R = T_a (S_P - S_R)$*. A Combustion Exergy Efficiency can be calculated by an indirect approach, as* $\eta_{ind} = 1 - EXD_R / EX_{in}$

---

[29] Consequently the element ΔG_{f0} are not zero and must be explicitly accounted; but the results of the sum ΔG_0 is the same as was calculated before from JANAF table data, referring to combustion in pure oxygen.

Figure 13 shows a parametric analysis of the combustion exergy efficiency as a function of the reactants pre-heating (a very effective measure to reduce irreversibilities).

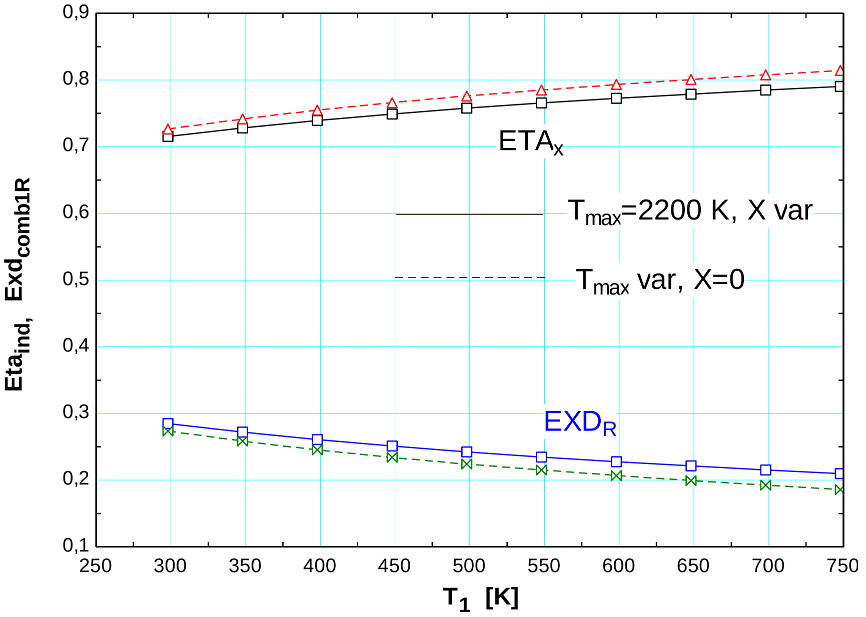


Figure 13 – Combustion exergy efficiency and destruction as a function of reactants pre-heating; Fixed Products T = 2200K or fixed excess air (stoichiometric, X = 0)

Figure 14 shows theeffect of dilution (X > 0) (reactants at $T_1 = 298$ *K). It is clear that stoichiometric combustionis the best option.*

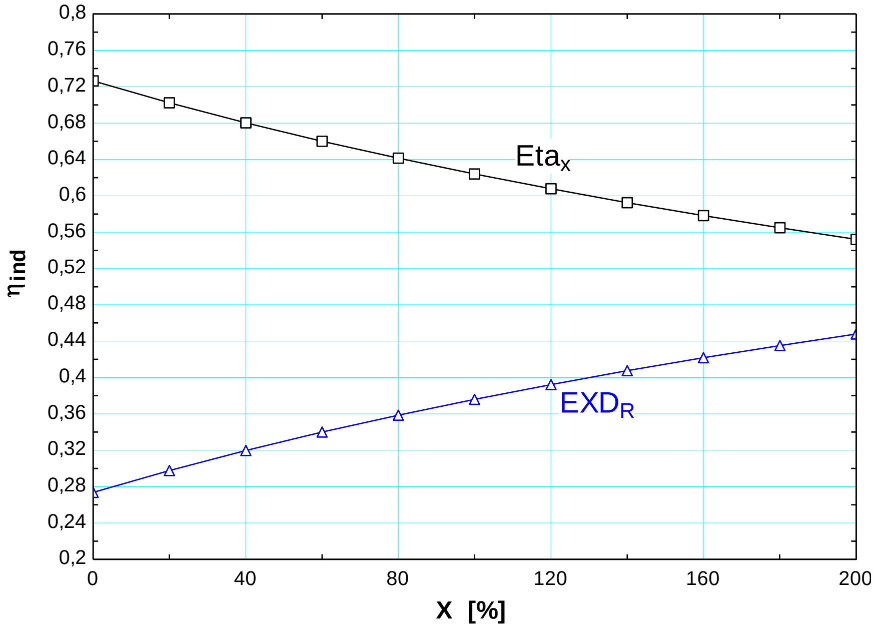


Figure 14 – Exergy efficiency and destruction of methane combustion, reactants $T_1 = 298$*K, with variable excess air.*

*Final statements about improving **combustion processes**:*

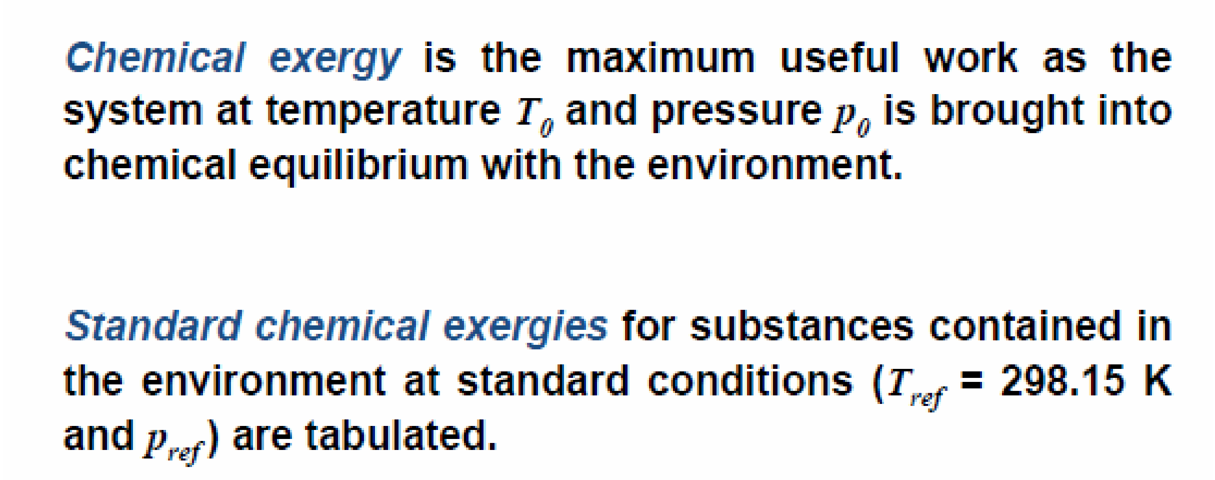
a) *From the thermodynamics point of view, combustion in pure oxygen or oxygen-enriched air is not a good practice, asit icreases the exergy destruction (even not considering the exergy spent for producing oxygen). Instead, **reactants pre-heating** is recommended.*

b) *Further reduction of combustion irreversibilities can be obtained substituting simple combustion chambers/reactors with more compelx **high-temperature chemical reactors** (for example, Solid-Oxyde Fuel Cells – SOFC– used as toppers for gas turbine cycles)*

c) *Improvements in overall exergy efficiency can be sought in **chemically-recuperated power cycles**, which allow to reduce the combustion irreversibilities through preparation of reactants(pre-heating and chemical recuperation)*

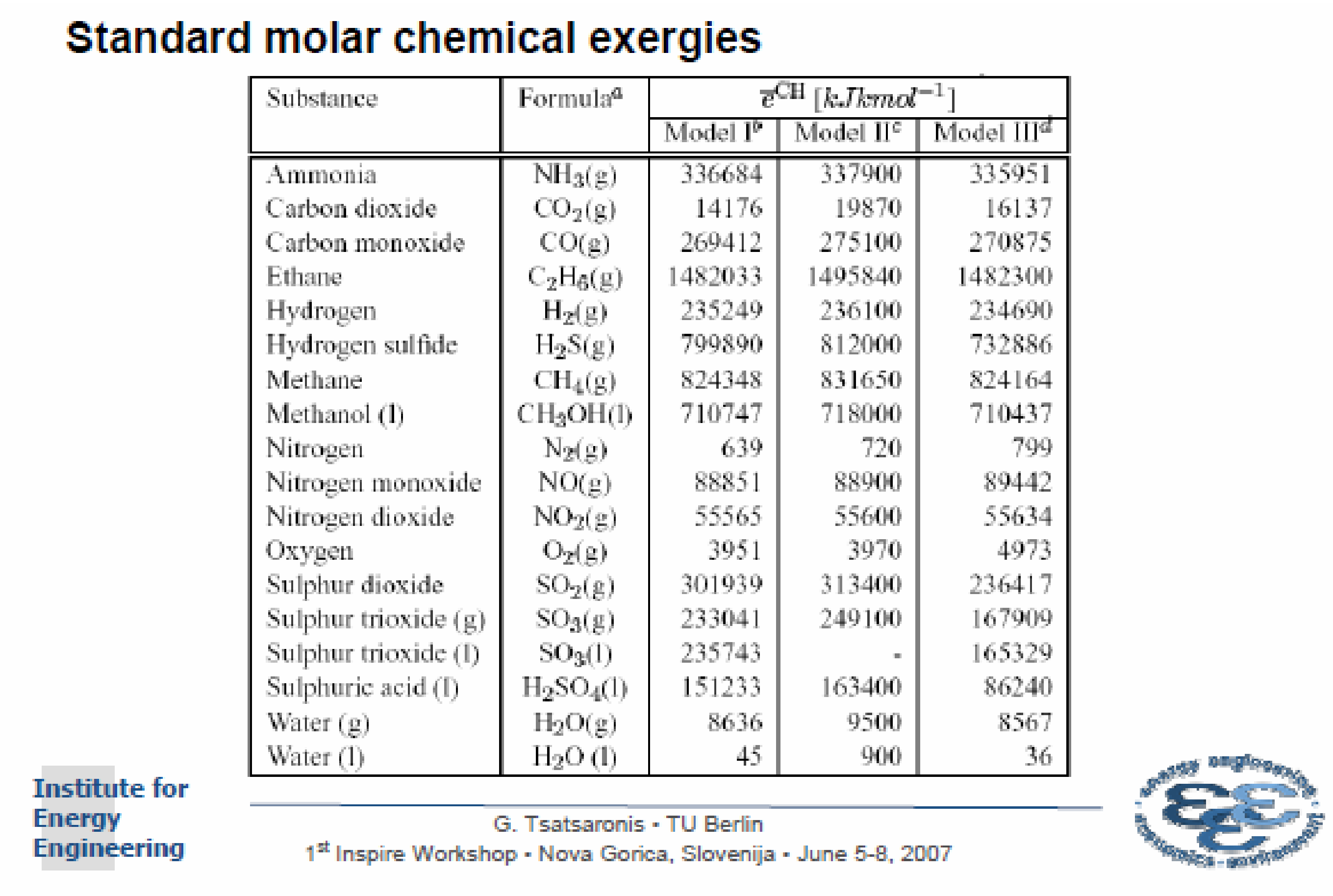
d) *Referring to fuels different from pure Methane, better exergy efficiencies (lower exergy destructions in combustion) can be achieved when using **low-BTU fuels** in nearly-stoichiometric conditions (this allows to control the final temperature with the lower heating value rather than by means of dilution with air, considering the materials constraints). Combustion irreversibilities for fuels having low calorific values are smaller.*

Chemical Exergy (3)– Summary



Chemical exergy is the maximum useful work as the system at temperature T_0 and pressure p_0 is brought into chemical equilibrium with the environment.

Standard chemical exergies for substances contained in the environment at standard conditions (T_{ref} = 298.15 K and p_{ref}) are tabulated.



Standard molar chemical exergies

Substance	Formula[a]	$\bar{e}^{CH}$ [kJkmol^{-1}]		
		Model I[b]	Model II[c]	Model III[d]
Ammonia	$NH_3(g)$	336684	337900	335951
Carbon dioxide	$CO_2(g)$	14176	19870	16137
Carbon monoxide	$CO(g)$	269412	275100	270875
Ethane	$C_2H_6(g)$	1482033	1495840	1482300
Hydrogen	$H_2(g)$	235249	236100	234690
Hydrogen sulfide	$H_2S(g)$	799890	812000	732886
Methane	$CH_4(g)$	824348	831650	824164
Methanol (l)	$CH_3OH(l)$	710747	718000	710437
Nitrogen	$N_2(g)$	639	720	799
Nitrogen monoxide	$NO(g)$	88851	88900	89442
Nitrogen dioxide	$NO_2(g)$	55565	55600	55634
Oxygen	$O_2(g)$	3951	3970	4973
Sulphur dioxide	$SO_2(g)$	301939	313400	236417
Sulphur trioxide (g)	$SO_3(g)$	233041	249100	167909
Sulphur trioxide (l)	$SO_3(l)$	235743	-	165329
Sulphuric acid (l)	$H_2SO_4(l)$	151233	163400	86240
Water (g)	$H_2O(g)$	8636	9500	8567
Water (l)	$H_2O(l)$	45	900	36

Institute for Energy Engineering

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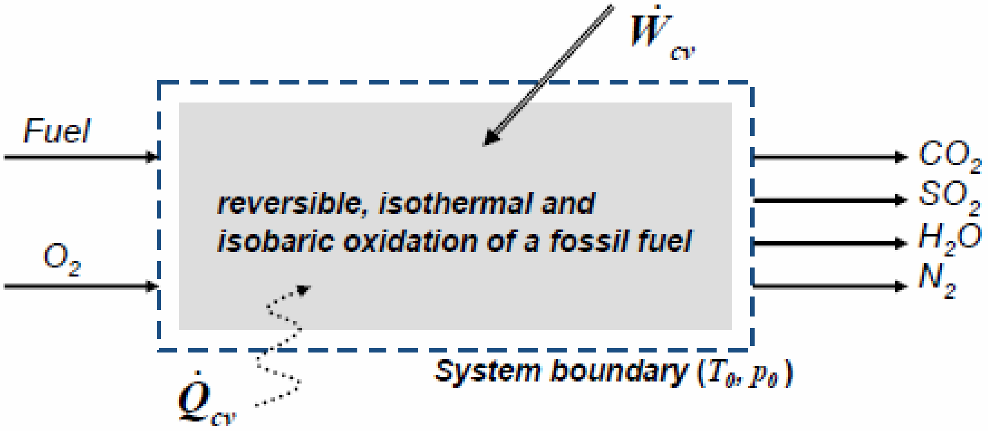


$$\bar{e}_f^{CH} = -\left(\Delta\bar{h}_R - T_0\Delta\bar{s}_R\right) + \Delta\bar{e}^{CH} = -\Delta\bar{g}_R + \Delta\bar{e}^{CH}$$

$$\Delta\bar{h}_R = \sum_i \nu_i \bar{h}_i = -\bar{h}_f + \sum_k \nu_k \bar{h}_k = -\overline{HHV}$$

$$\Delta\bar{s}_R = \sum_i \nu_i \bar{s}_i = -\bar{s}_f + \sum_k \nu_k \bar{s}_k$$

$$\Delta\bar{g}_R = \Delta\bar{h}_R - T_0 \Delta\bar{s}_R$$

$$\Delta\bar{e}^{CH} = \sum_k \nu_k \bar{e}_k^{CH}$$

where $i = f, O_2, CO_2, H_2O, SO_2, N_2$
$k = O_2, CO_2, H_2O, SO_2, N_2$
ν_i *and* $\nu_k \geq 0 : CO_2, H_2O, SO_2, N_2$
ν_i *and* $\nu_k < 0 : f, O_2$

Chemical exergy of an ideal mixture of N ideal gases

$$\boxed{\bar{e}^{CH}_{M,ig} = \sum_{k=1}^{N} x_k \bar{e}_k^{CH} + \bar{R} T_0 \sum_{k=1}^{N} x_k \, ln(x_k)}$$

Notice 1 : Here the Enthalpy of reaction is assimilated to the Higher Heating Value (American style), while in Eq. 37 it was:

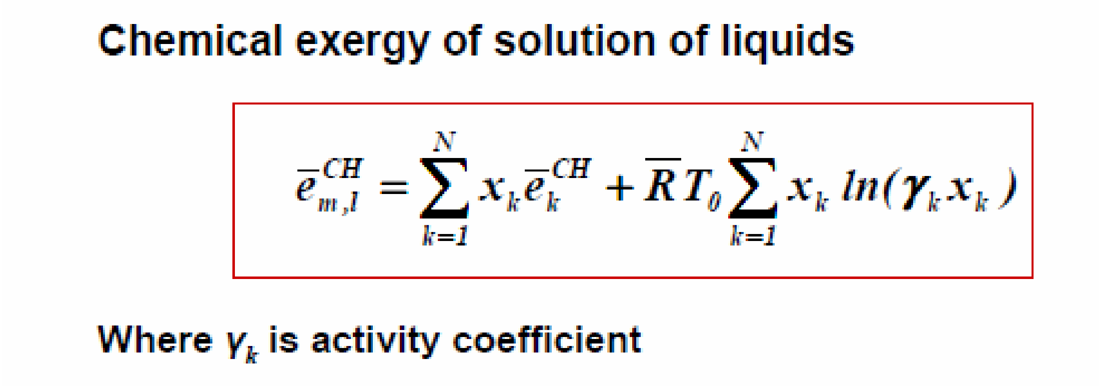
$$H_{ci} = -\frac{\Delta H_r^o}{M_f}$$

Notice 2: $\Delta\bar{e}^{CH}$ is the same as $\tilde{\varepsilon}_{0k} = \tilde{R} T_a ln \frac{p_a}{p_{a0i}}$ (50)

The final result is the same as:

$$\tilde{\varepsilon}_0 = -\Delta\tilde{h}_0 + T_a \Delta\tilde{s}_0 + \tilde{R} T_a \left(x_{O_2} \ln \frac{p_{a0O_2}}{p_a} - \sum_i x_i \ln \frac{p_{a0i}}{p_a} \right) \tag{51}$$

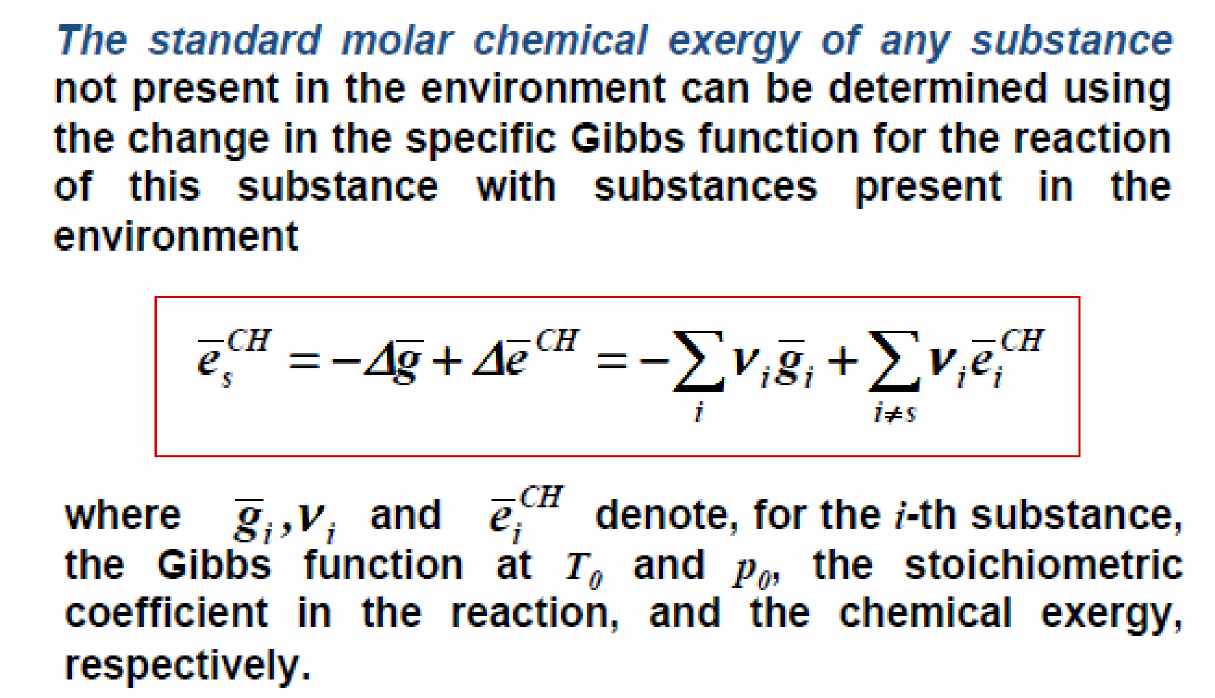
Extension to liquid solutions[30]:



Chemical exergy of solution of liquids

$$\boxed{\bar{e}^{CH}_{m,l} = \sum_{k=1}^{N} x_k \bar{e}^{CH}_k + \bar{R} T_0 \sum_{k=1}^{N} x_k \, ln(\gamma_k x_k)}$$

Where γ_k is activity coefficient



The standard molar chemical exergy of any substance not present in the environment can be determined using the change in the specific Gibbs function for the reaction of this substance with substances present in the environment

$$\boxed{\bar{e}^{CH}_s = -\Delta\bar{g} + \Delta\bar{e}^{CH} = -\sum_i \nu_i \bar{g}_i + \sum_{i\neq s} \nu_i \bar{e}^{CH}_i}$$

where $\bar{g}_i, \nu_i$ and $\bar{e}^{CH}_i$ denote, for the *i*-th substance, the Gibbs function at T_0 and p_0, the stoichiometric coefficient in the reaction, and the chemical exergy, respectively.

Chemical Exergy (4). Technical Fuels.

Real fuels are a mix of several complex chemical compounds. Consequently, it is difficult to calculate their chemical exergy with the formulas exemplified for a pure substance (CH_4). Therefore, a correlation approach has been introduced to valuate theri Chemical Exergy, taking as the starting point the Lowe Calorific Value:

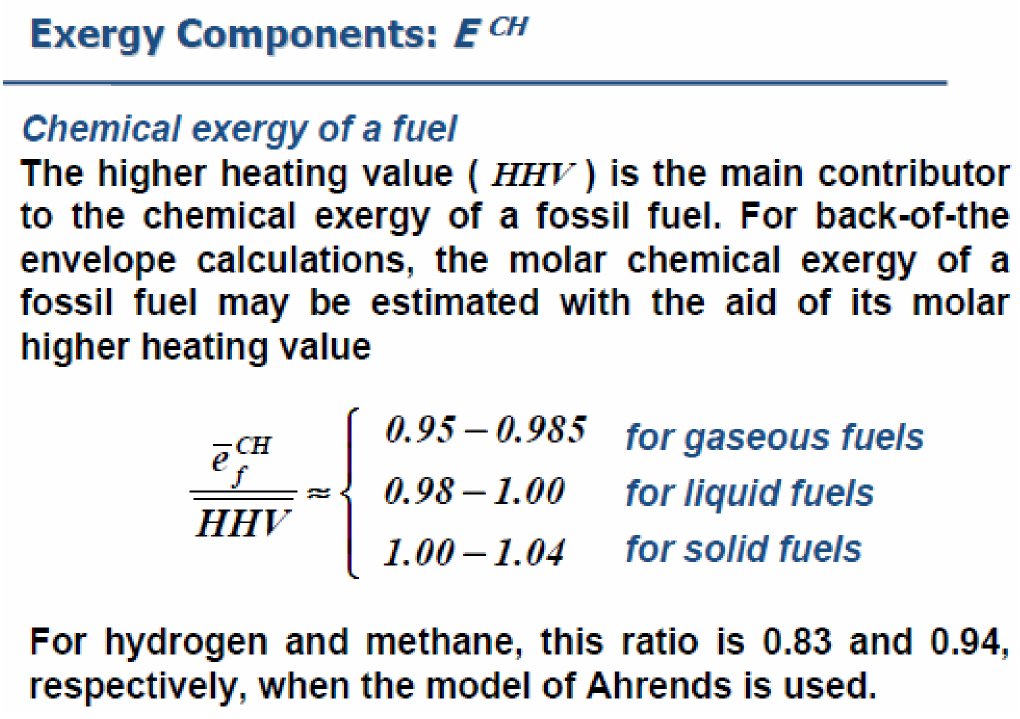
---

[30] E.g. ionic liquids, CO2 separation through alkaline reactants/amines; evaluation of exergy of geothermal brines containing H2O, CO2, salts and non-condensable gases.

$$\varphi = \frac{\varepsilon_0}{H_{ci}} \qquad (51)$$

The approach to expressing φis similar to what is used for Energy calculations (e.g. DuLong formula for H_{ci}).

φdepends largely on the chemical composition, considering the strength of the bonds links within the hydrocarbon chain. Depending on the specific fuelsthe C-H bonds have different relevance in the evaluation of φ: for example, for sub-bituminous coals the cyclo-paraffinic bonds (long C-H chains) determine a smaller contribution with respect to other fuels.



Exergy Components: E^{CH}

Chemical exergy of a fuel

The higher heating value (HHV) is the main contributor to the chemical exergy of a fossil fuel. For back-of-the envelope calculations, the molar chemical exergy of a fossil fuel may be estimated with the aid of its molar higher heating value

$$\frac{\bar{e}_f^{CH}}{\overline{\overline{HHV}}} \approx \begin{cases} 0.95-0.985 & \text{for gaseous fuels} \\ 0.98-1.00 & \text{for liquid fuels} \\ 1.00-1.04 & \text{for solid fuels} \end{cases}$$

For hydrogen and methane, this ratio is 0.83 and 0.94, respectively, when the model of Ahrends is used.

Formulas of Szargut e Styrylska

Szargut and Styrylska proposed a statistical approach to the calculation of φ, based on the atomic ratios N_H/N_C, N_O/N_C, N_N/N_C e $N_S/N_C$when the chimica composition is known; and on the mass fractions for fuels where only the final mass composition is known[31].

Gaseous fuels

$$\varphi = 1.0334 + 0.0183\frac{N_H}{N_C} - 0.0694\frac{1}{N_c}$$

Liquids Hydrocarbons

$$\varphi = 1.0406 + 0.0144\frac{N_H}{N_C}$$

Solid Hydrocarbons

$$\varphi = 1.0435 + 0.0159\frac{N_H}{N_C}$$

Liquids with C,H,O (e.g. Alcohols,…)

$$\varphi = 1.0374 + 0.0159\frac{N_H}{N_C} + 0.0567\frac{N_O}{N_C}$$

---

[31] As resulting from a Mass Spectrometer or Thermogravimetric analysis

Solids with C,H,O:

$$\varphi = 1.0438 + 0.0158\frac{N_H}{N_C} + 0.0813\frac{N_O}{N_C};\ \frac{N_O}{N_C} \le 0.5$$

$$\varphi = \frac{\left[1.0414 + 0.0177\frac{N_H}{N_C} - 0.3328\frac{N_O}{N_C}\left(1 + 0.0537\frac{N_H}{N_C}\right)\right]}{1 - 0.4021\frac{N_O}{N_C}};\quad \frac{N_O}{N_C} \le 2$$

Liquids with C,H,O,S:

$$\varphi = 1.0407 + 0.0154\frac{N_H}{N_C} + 0.0562\frac{N_O}{N_C} + 0.5904\frac{N_S}{N_C}\left(1 - 0.175\frac{N_H}{N_C}\right)$$

Solids with C,H,O,N[32]:

$$\varphi = 1.0437 + 0.0140\frac{N_H}{N_C} + 0.0968\frac{N_O}{N_C} + 0.0467\frac{N_N}{N_C};\ \frac{N_O}{N_C} \le 0.5$$

$$\varphi = \frac{\left[1.044 + 0.016\frac{N_H}{N_C} - 0.3493\frac{N_O}{N_C}\left(1 + 0.0531\frac{N_H}{N_C}\right)\right] + 0.0493\frac{N_N}{N_C}}{1 - 0.4124\frac{N_O}{N_C}}$$

$$\boxed{\frac{N_O}{N_C} \le 2}$$

---

[32] Coals, Petcokes,…

Bituminous coal, lignite, turf (SS-coal)

$$\varphi = 1.0437 + 0.1896\frac{H}{C} + 0.0617\frac{O}{C} + 0.0428\frac{N}{C}$$

Wood (SS-wood)

$$\varphi = \frac{\left[1.0412 + 0.216\frac{H}{C} - 0.2499\frac{O}{C}\left(1 + 0.7884\frac{H}{C}\right)\right] + 0.0450\frac{N}{C}}{1 - 0.3035\frac{O}{C}}$$

Technical liquid fuel (SS-liquid)

$$\varphi = 1.0401 + 0.1728\frac{H}{C} + 0.0432\frac{O}{C} + 0.2169\frac{S}{C}\left(1 - 2.0628\frac{H}{C}\right)$$

Shieh-Fan Formulation

The Shieh-Fan approach is particularly recommended for Refuse-Derived Fuels (RDF), asit contains contributions from halogens as are often determined by the presence of plastics[33].

The Shieh-Fan approach connects to the exact way of calculating ΔG_o:

$$\Delta G_r^0 = \Delta H_r^0 - T_a \Delta S_r^0 \qquad (52)$$

Using the heat of reaction ΔH_r^0, which can be either calculated or approximated from H_{ci} correlations[34]; ΔS_r^0 is the entropy variation (products-reactants) of the chemical reaction, which according to Shieh and Fan can be evaluated from the following equation:

$$\begin{aligned}\Delta S_r^0 = {} & 0.1718[C] - 3.86[H] + 1.5314[O] + 0.3217[S] + 1.634[N] + \\ & + 2.389[F] + 1.369[Cl] + 0.6426[Br] + 0.4195[I] - s_{fuel}^0\end{aligned} \qquad (53)$$

---

[33] Definitely positive in terms of raisng H_{ci}.

[34] Modified DuLong formulas for RDF, containing Cl and F terms

Terms in square brackets [ ] represent the molar composition of the fuel.

The following table shows an application of the SS/SF formulas for some typical fuels (natural or synthetic).

Table 4 - Comparison of different estimates for H_{ci} and φ

	RDF	Wood Chips	Sorghum (fiber)	Ensyn Synfuel
Composizione				
C [%]	**44.2**	**46.2**	**44.8**	**56.4**
H [%]	**6.6**	**5.8**	**6.3**	**6.2**
N [%]	**0.5**	**0.2**	**1.1**	**0.2**
S [%]	**0.4**	**0.3**	**0.14**	**< 0.01**
O [%]	**32.0**	**37.7**	**52.34**	**37.09**
Cl [%]			**0.625**	
F [%]			**0.0236**	
Ash				**0.1**
Potere calorifico superiore [kJ/kg]				
Hcs (exp.)	**18800**	**17600**	**16530**	**23000**
Hci (exp)	**17375**	**16350**	**15170**	**21660**
Hci (S-F)	**17990**	**16440**	**14200**	**20550**
φ (SS-Carbone)	**1.117**			
φ (SS- Legna)		**1.122**	**1.159**	
φ (SS-Liquidi)				**1.0875**
φ (SF+HCl_exp)	**1.231**	**1.232**	**1.187**	**1.142**

Ensyn Synfuel: liquid biofuel (oil) obtained from fast pyrolysis process of agricultural biomass.

System Analysis - Component Exergy Balances

Evaluating materials and exergy streams crossing the boundaries of all plant components is the preliminary step of an exergy-based analysis.

After that, there are several methods for conducting an exergy analysis. The following approach introduces a clear conceptual definition of exergy fuel and exergy product from the component functional point of view, which is essential for further developments (**Exergo-Economics and Exergo-Environmental Analysis**).

The product and fuel[35] of the component are defined by considering the desired results produced by a component and the exergy resources consumed to generate the results, respectively.

In the definition of fuel and product, it is meaningful and appropriate to operate with exergy differences associated with each material stream between inlet and outlet. Exergy differences should be applied to all exergy streams associated with a change of physical exergy and to exergy streams associated with the conversion of chemical exergy. *Only if the purpose of a component is to provide at the outlet a different type of chemical exergy than is available at the inlet, no differences of chemical exergies are used.*

- Exergy streams associated with energy streams (e.g. heat or work) appear either at the component inlet (in this case they represent or are part of the fuel), or at the outlet (in this case they are part of the product).

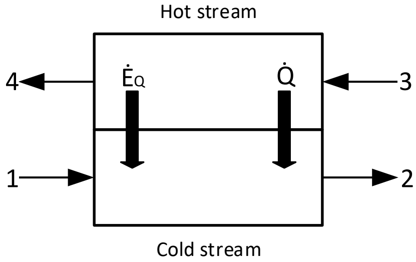
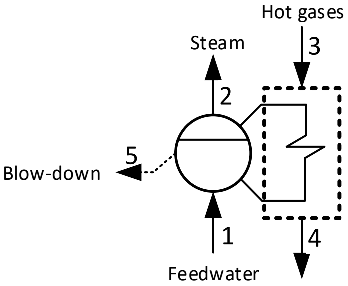
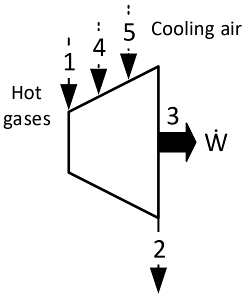
---

[35] The definitions of component exergy product and fuel, and general guidelines to this approach were proposed by Lazzaretto, A., Tsatsaronis, G., On the Quest for Objective Equations in Exergy Costing, Proceedings of the ASME Advanced Energy Systems Division," *ASME,* AES-Vol. 37, pp. 197-210, 1997

- The product of the component consists of all the exergy values to be considered at the outlet (including the exergy of energy streams generated in the component) and all the exergy increases between inlet and outlet.

- The fuel of the component consists of all the exergy values to be considered at the inlet (including the exergy of energy streams supplied to the component) and all the exergy decreases between inlet and outlet.

Some relevant cases for calculation of fuel and product exergy rates for typical components are listed in the following Table :

	**Heat Exchanger** $\dot{E}_P = \dot{E}_2 - \dot{E}_1$ $\dot{E}_F = \dot{E}_3 - \dot{E}_4$
	**Evaporator (including steam drum)** $\dot{E}_P = \dot{E}_2 + \dot{E}_5 - \dot{E}_1$ $\dot{E}_F = \dot{E}_3 - \dot{E}_4$
	**Turbine or expander** (multiple inputs) $\dot{E}_P = \dot{E}_3 = \dot{W}$ $\dot{E}_F = \dot{E}_1 + \dot{E}_4 + \dot{E}_5 - \dot{E}_2$

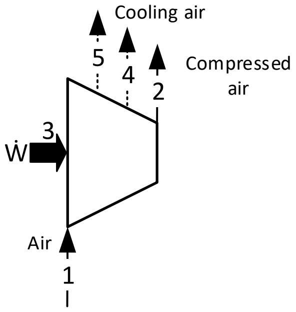
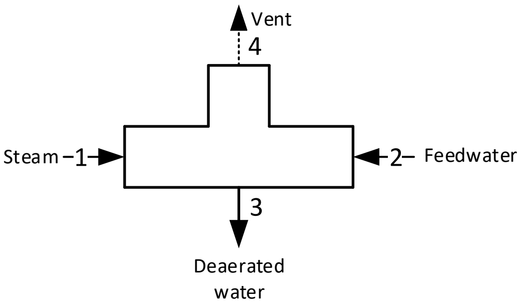
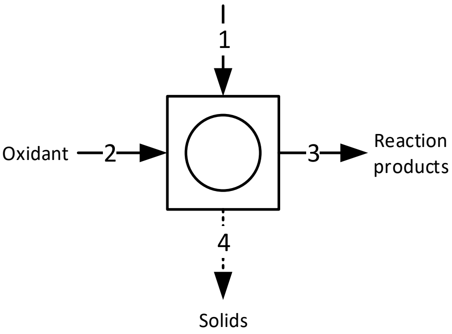
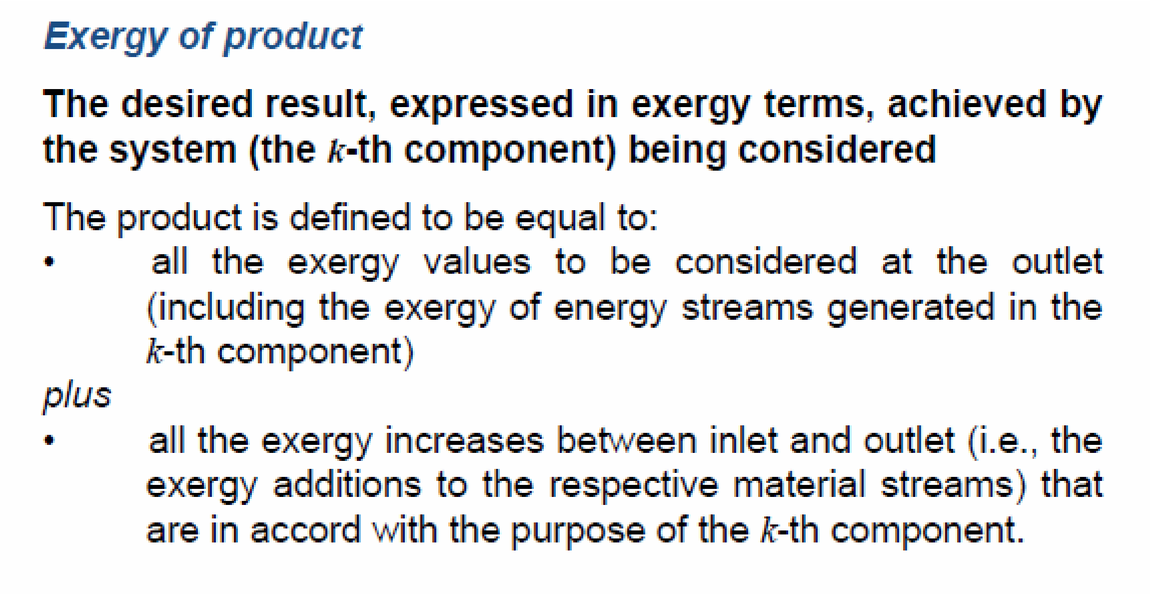
	**Compressor, pump or fan** (multiple outputs) $\dot{E}_P = \dot{E}_2 + \dot{E}_4 + \dot{E}_5 - \dot{E}_1$ $\dot{E}_F = \dot{E}_3 = \dot{W}$
	**MFH - Deaerator**[36] $\dot{E}_P = \dot{m}_2(e_3 - e_2)$ $\dot{E}_F = \dot{m}_1 e_1 - (\dot{m}_1 - \dot{m}_4)e_3 - \dot{m}_4 e_4$
	**Combustion chamber** $\dot{E}_P = \dot{E}_3 - \dot{E}_2$ $\dot{E}_F = \dot{E}_1 - \dot{E}_4$

Table 5: Fuel and products definitions.



Exergy of product

The desired result, expressed in exergy terms, achieved by the system (the *k*-th component) being considered

The product is defined to be equal to:

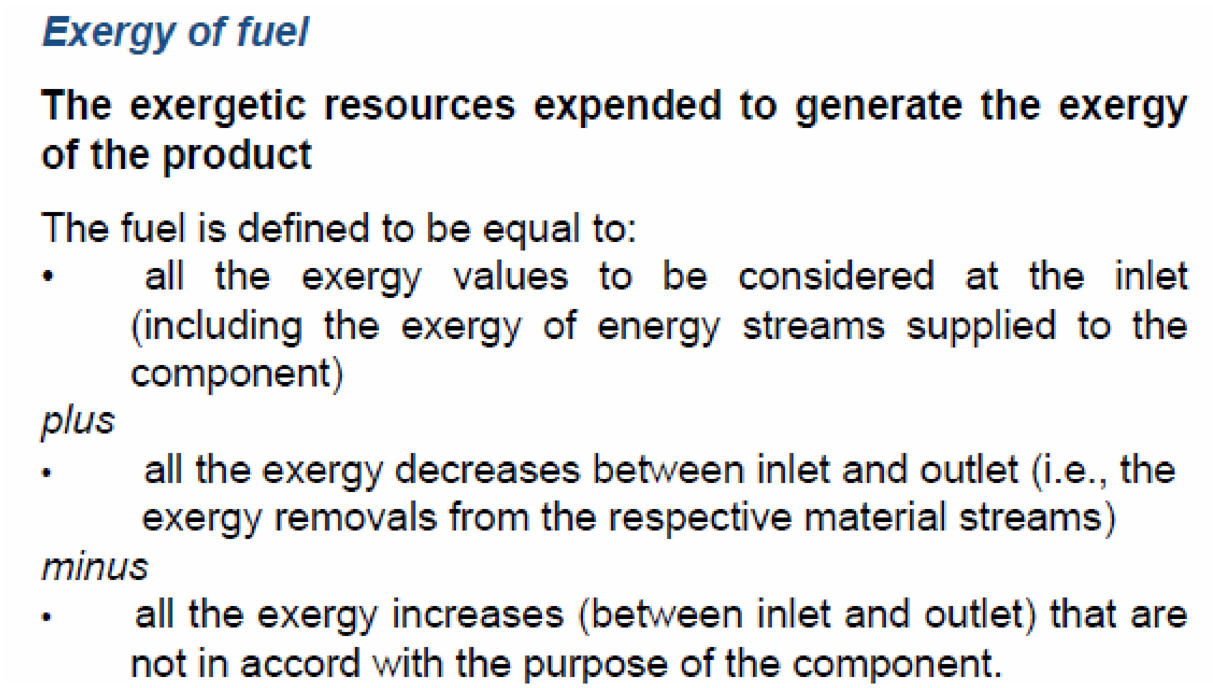
- all the exergy values to be considered at the outlet (including the exergy of energy streams generated in the *k*-th component)

plus

- all the exergy increases between inlet and outlet (i.e., the exergy additions to the respective material streams) that are in accord with the purpose of the *k*-th component.

---

[36] The purpose is removing non-condensible gases from the feedwater stream



Exergy of fuel

The exergetic resources expended to generate the exergy of the product

The fuel is defined to be equal to:

- all the exergy values to be considered at the inlet (including the exergy of energy streams supplied to the component)

plus

- all the exergy decreases between inlet and outlet (i.e., the exergy removals from the respective material streams)

minus

- all the exergy increases (between inlet and outlet) that are not in accord with the purpose of the component.

Non-dimensional Component Exergy Performance Indicators

Starting from the component exergy balances and having defined the Component Product and Fuel, it is possible to define the Component Exergy Efficiency, and to get back at the overall system performance considering the full system as an assembly of interconnected components.

The Exergy Efficiency for the *k-th* component, ε_k is defined by the following equations:

$$\varepsilon_k = \frac{\dot{E}_{P,k}}{\dot{E}_{F,k}} = 1 - \frac{\dot{E}_{D,k}}{\dot{E}_{F,k}} \qquad (52)$$

The Exergy Efficiency of the overall system ε_{tot} is defined by[37]:

$$\varepsilon_{tot} = \frac{\dot{E}_{P,tot}}{\dot{E}_{F,tot}}$$

$$= 1 - \frac{\dot{E}_{D,tot} + \dot{E}_{L,tot}}{\dot{E}_{F,tot}} \qquad (54)$$

The exergy efficiency is the only variable that characterizes the performance of a component from the thermodynamics point of view. It also permits to compare components operating under similar conditions in the considered system or in a different one.

In order to identify the most significant exergy destructions within an energy conversion system an additional parameter is needed, which is named the Component Exergy Destruction Ratio:

$$y_k = \frac{\dot{E}_{D,k}}{\dot{E}_{F,tot}} \qquad (55)$$

y_k can be used for allocating the total exergy destruction among the components, and for illustrating the distribution of thermodynamic inefficiencies through the system.

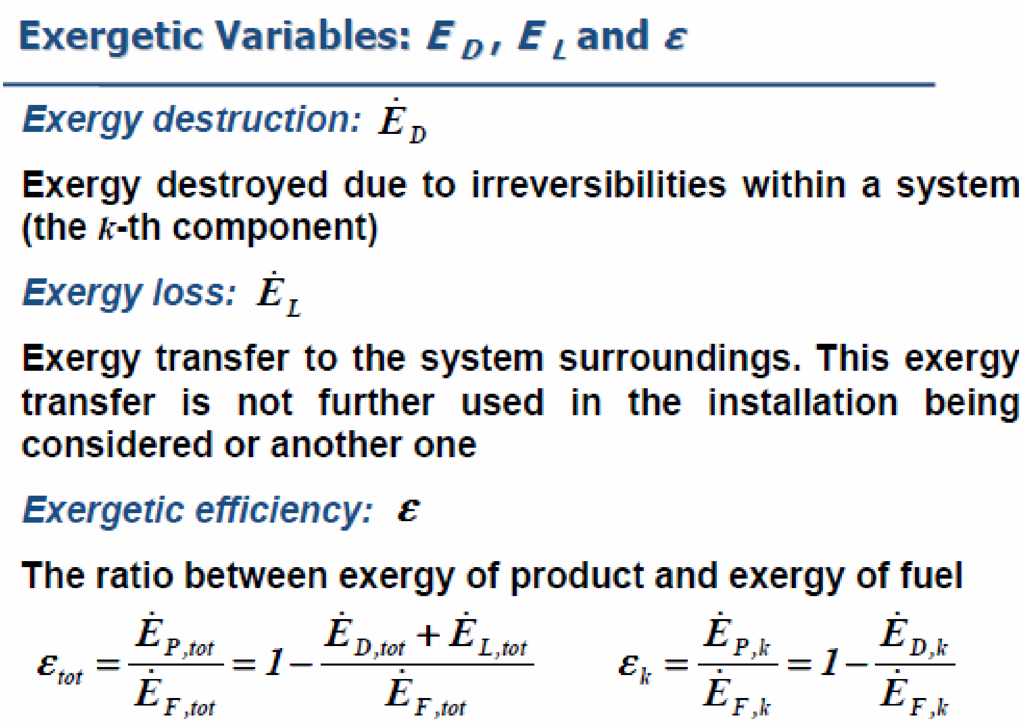
Not all the components have the same impact on the overall functioning of a plant: some devices have a dominant role in determining the overall exergy performance. The exergy efficiency and the exergy destruction ratio help to recognize the components whose improvement can result in significant benefits in terms of performance.

---

[37] Please notice that while ε_k contains only the Exergy Destruction, which is attributed to the component; ε_{tot} contains both the overall system Exergy Destruction (which is the sum of the exergy destructions for all components), and the overall system Exergy Loss. This is a classical approach: Losses are retained as functional to operation of the system, and are NOT attributed to defect of component performance. This is not the only possible approach, but is is quite common.

The first step of the system exergy analysis is listing the system components in descending order according to the values of the exergy destruction ratio y_k.

In fact, it is right to first improve components showing the highest values of y_k since they are the main source of exergy destruction.



Exergetic Variables: E_D, E_L and ε

Exergy destruction: $\dot{E}_D$

Exergy destroyed due to irreversibilities within a system (the *k*-th component)

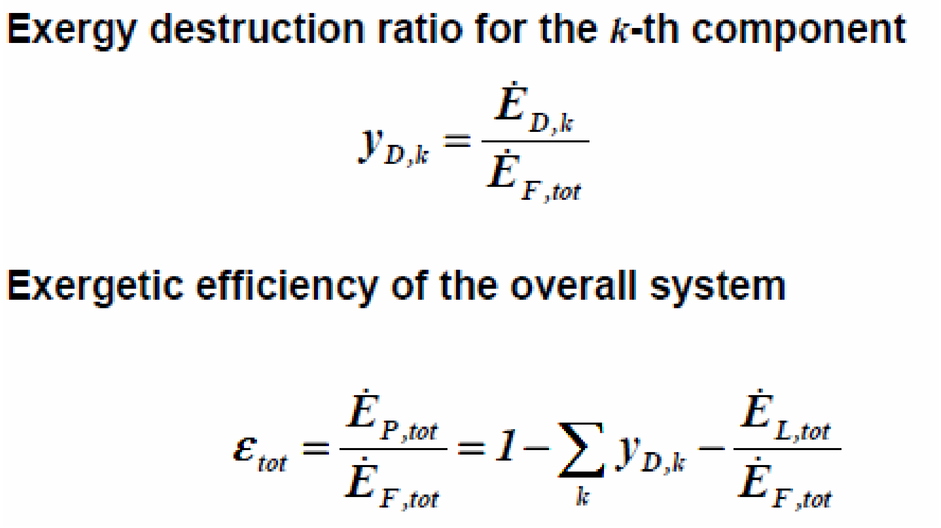
Exergy loss: $\dot{E}_L$

Exergy transfer to the system surroundings. This exergy transfer is not further used in the installation being considered or another one

Exergetic efficiency: ε

The ratio between exergy of product and exergy of fuel

$$\varepsilon_{tot} = \frac{\dot{E}_{P,tot}}{\dot{E}_{F,tot}} = 1 - \frac{\dot{E}_{D,tot} + \dot{E}_{L,tot}}{\dot{E}_{F,tot}} \qquad \varepsilon_k = \frac{\dot{E}_{P,k}}{\dot{E}_{F,k}} = 1 - \frac{\dot{E}_{D,k}}{\dot{E}_{F,k}}$$



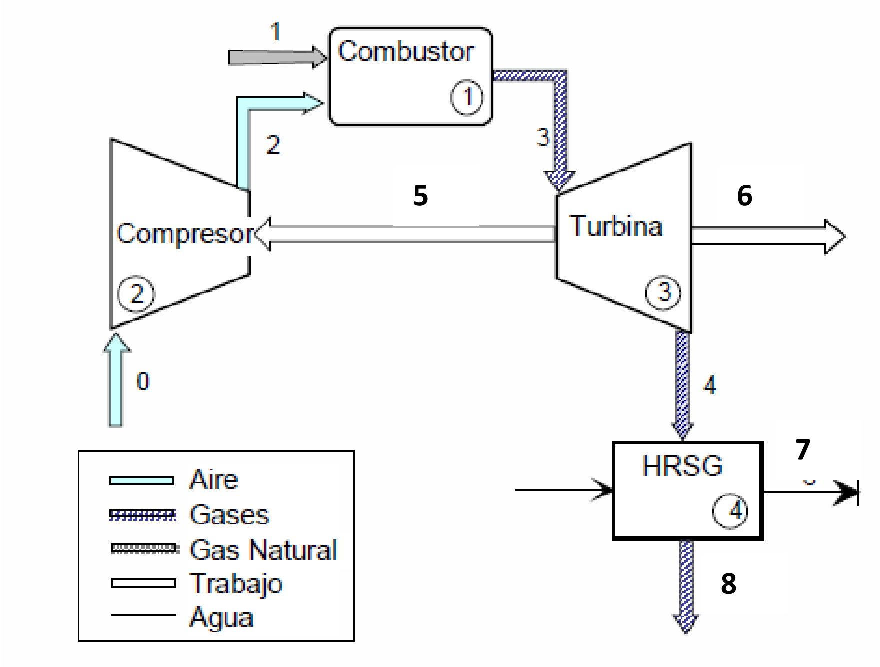
Exergy destruction ratio for the *k*-th component

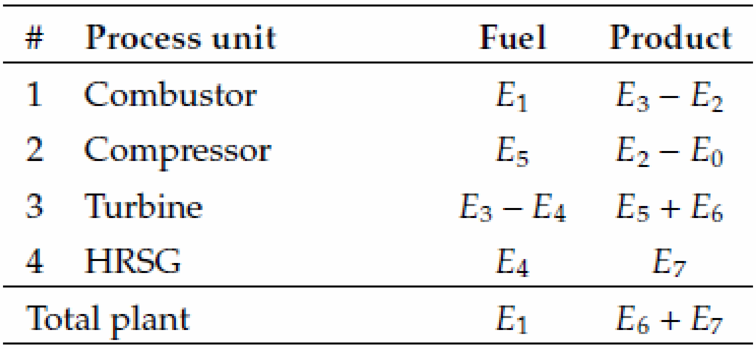
$$y_{D,k} = \frac{\dot{E}_{D,k}}{\dot{E}_{F,tot}}$$

Exergetic efficiency of the overall system

$$\varepsilon_{tot} = \frac{\dot{E}_{P,tot}}{\dot{E}_{F,tot}} = 1 - \sum_k y_{D,k} - \frac{\dot{E}_{L,tot}}{\dot{E}_{F,tot}}$$

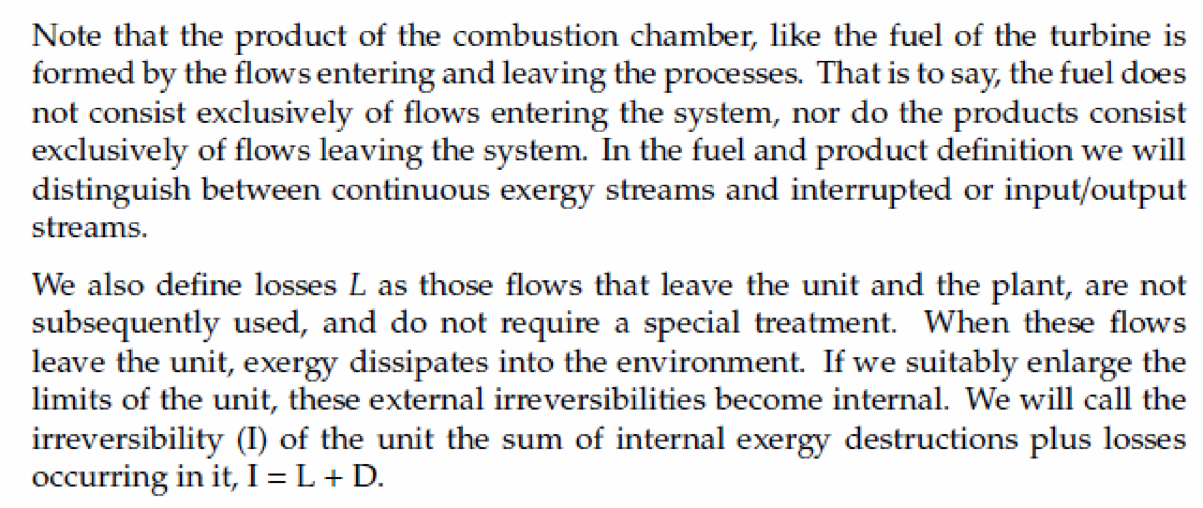
Examples





#	Process unit	Fuel	Product
1	Combustor	E_1	$E_3 - E_2$
2	Compressor	E_5	$E_2 - E_0$
3	Turbine	$E_3 - E_4$	$E_5 + E_6$
4	HRSG	E_4	E_7
Total plant		E_1	$E_6 + E_7$

Figure 15 - Gas Turbine CHP plant[38]



Note that the product of the combustion chamber, like the fuel of the turbine is formed by the flows entering and leaving the processes. That is to say, the fuel does not consist exclusively of flows entering the system, nor do the products consist exclusively of flows leaving the system. In the fuel and product definition we will distinguish between continuous exergy streams and interrupted or input/output streams.

We also define losses *L* as those flows that leave the unit and the plant, are not subsequently used, and do not require a special treatment. When these flows leave the unit, exergy dissipates into the environment. If we suitably enlarge the limits of the unit, these external irreversibilities become internal. We will call the irreversibility (I) of the unit the sum of internal exergy destructions plus losses occurring in it, I = L + D.

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[38] Torres, CT, Valero, A., Thermoeconomics PhD Course, 2005, CIRCE.

We will call productive units those whose objective is to transfer the exergy contained in the fuels to the products. The fuel-product definitions for productive units should be chosen such that the equation F - P = I is an expression of each exergy balance. The exergy efficiency of these units is defined as:

$$\varepsilon = \frac{\text{Exergy of useful product}}{\text{Exergy of resources}} = \frac{P}{F} \qquad 0 < \varepsilon < 1$$

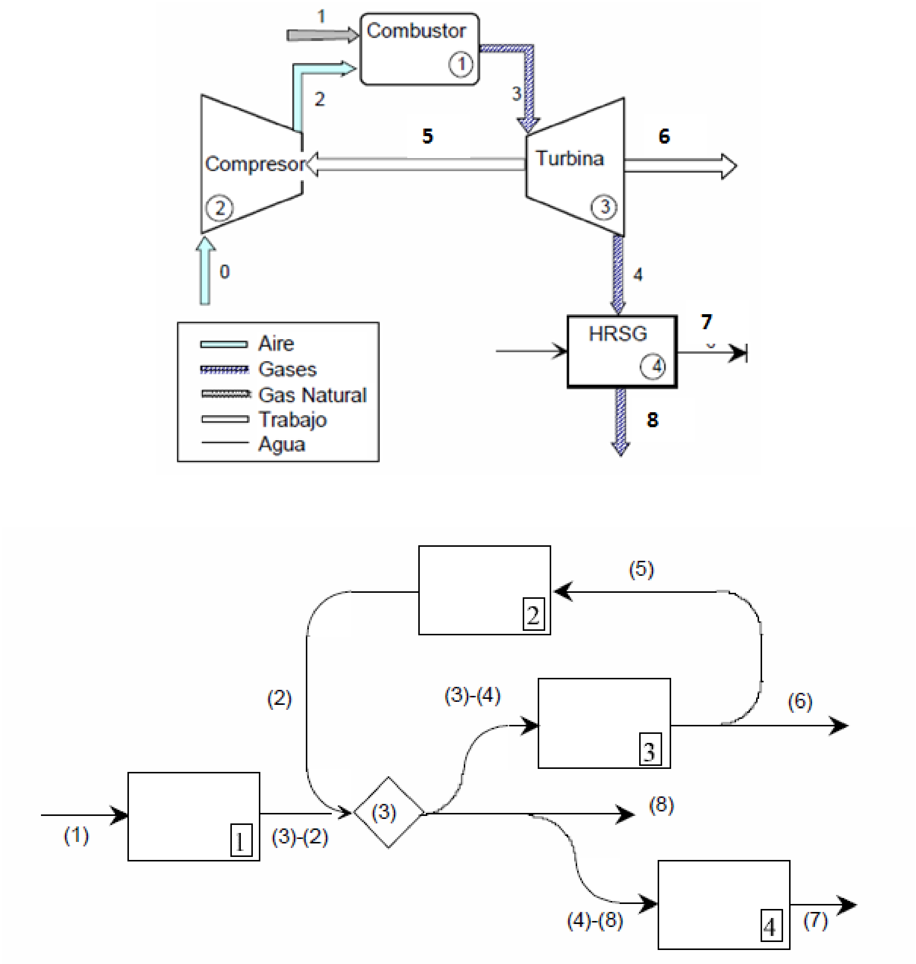

Figure 16 – Productive structure of the GT CHP plant[39]

Note that in most of cases the flows appearing in the productive structure are fictitious and are not necessarily physical flows. While each plant has only one physical structure to describe the physical relations between the process units, various productive structures can be defined depending on the fuel and product definitions as well as decisions on how the plant resources are distributed among the process units. Figure 2 shows the productive structure corresponding to a specific thermoeconomic model, i.e. corresponding to a specific Fuel-Product definition (see table 1.1). Depending on the thermoeconomic model definition the productive structure varies, obtaining thus as many productive structures as thermoeconomic model definitions.

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[39] Notice loop introduced by direct transfer of compressor work through the GT shaft, E_5.

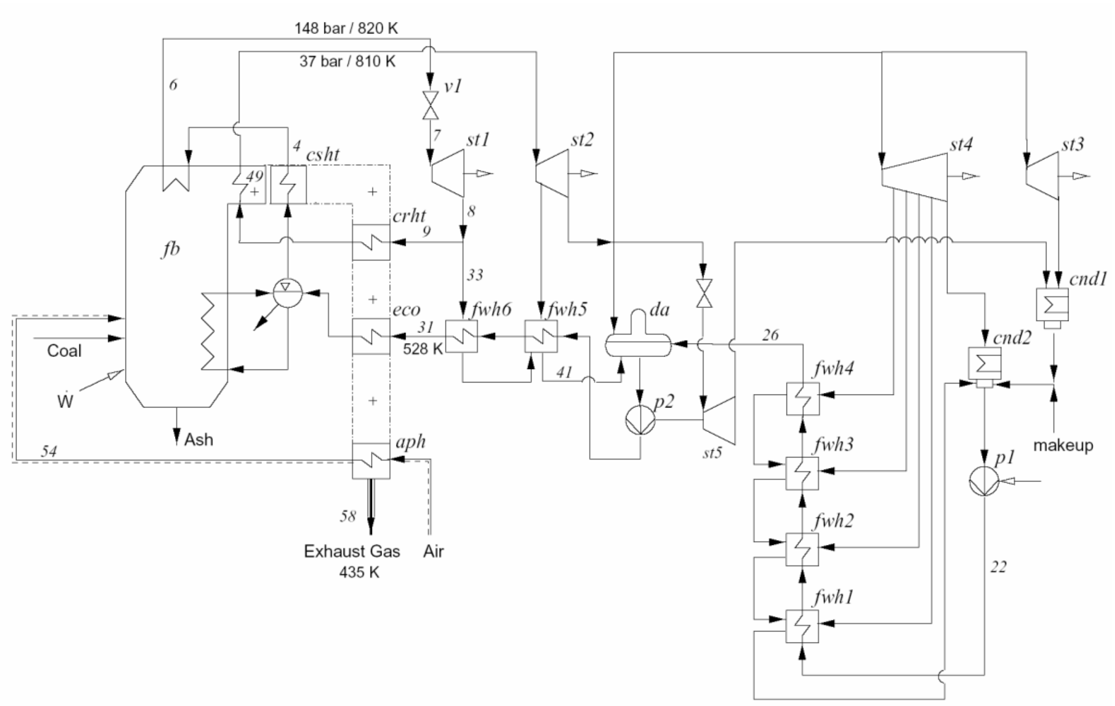

Fig. 17 - 400 MW Coal-Fired Subcritical Power Plant

Component	ID	$\dot{E}_{F,k}$ [MW]	$\dot{E}_{P,k}$ [MW]	ε_k [%]	$\dot{E}_{D,k}$ [MW]	$y_{D,k}$ [%]
Fossil boiler	fb	775.63	328.59	42.4	447.04	42.78
Convective superheater	$csht$	118.22	88.76	75.1	29.45	2.82
Air preheater	aph	42.75	25.58	59.8	17.18	1.64
Economizer	eco	54.55	43.13	79.1	11.42	1.09
Convective reheater	$crht$	36.40	28.59	78.5	7.81	0.75
LP steam turbine	$st3$	132.96	125.83	94.6	7.14	0.68
HP steam turbine	$st1$	118.98	113.07	95.0	5.91	0.57
Generator	gen	407.84	402.54	98.7	5.30	0.51
IP steam turbine	$st2$	101.55	97.03	95.5	4.52	0.43
LP steam turbine	$st4$	75.88	71.92	94.8	3.96	0.38
Deaerator	da	18.99	16.57	87.3	2.42	0.23
LP feedwater heater	$fwh2$	10.48	8.10	77.3	2.38	0.23
HP feedwater heater	$fwh6$	29.84	28.05	94.0	1.79	0.17
Steam turbine	$st5$	10.05	8.31	82.7	1.74	0.17
LP feedwater heater	$fwh4$	12.46	11.00	88.3	1.46	0.14
HP feedwater heater	$fwh5$	11.99	10.88	90.7	1.11	0.11
Feedwater pump	$p2$	8.31	7.52	90.5	0.79	0.08
LP feedwater heater	$fwh1$	2.23	1.66	74.2	0.57	0.06
LP feedwater heater	$fwh3$	5.42	5.10	94.2	0.32	0.03
Condensate pump	$p1$	0.73	0.63	85.9	0.10	0.01
Overall plant	tot	1044.86	400.13	38.3	552.86	52.91

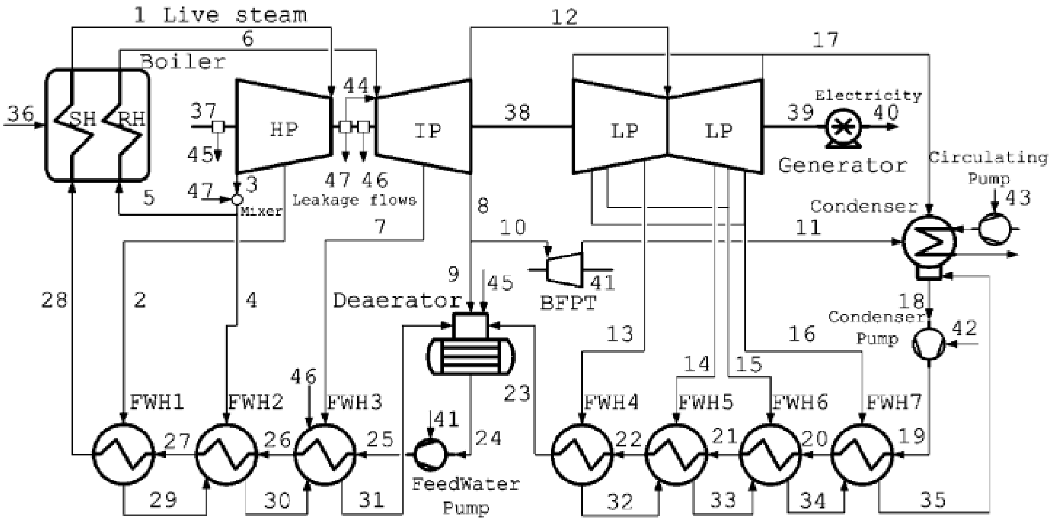

Figure 18 - Schematic diagram of steam power plant[40]

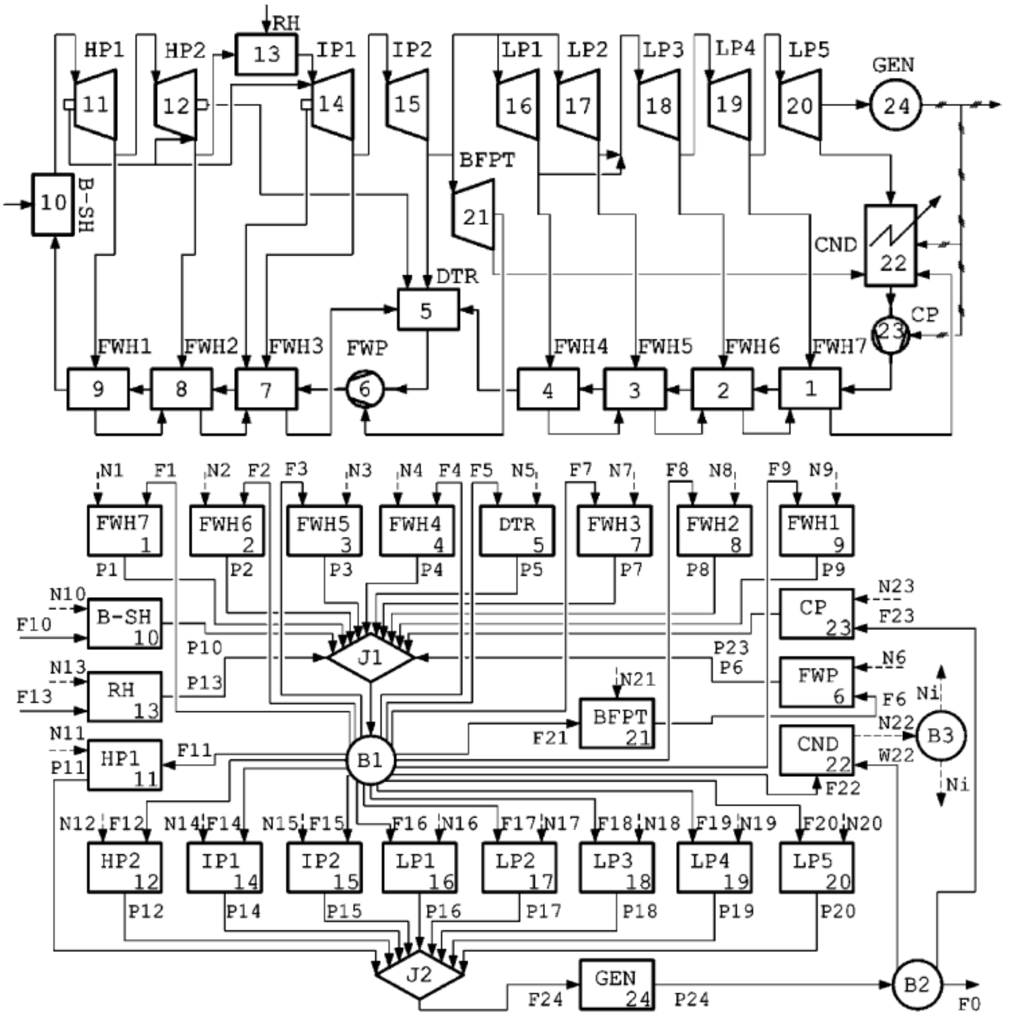

Figure 19 - Productive structure of steam power plant

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[40] C. Zhang et al. / Energy Conversion and Management 47 (2006) 817–843

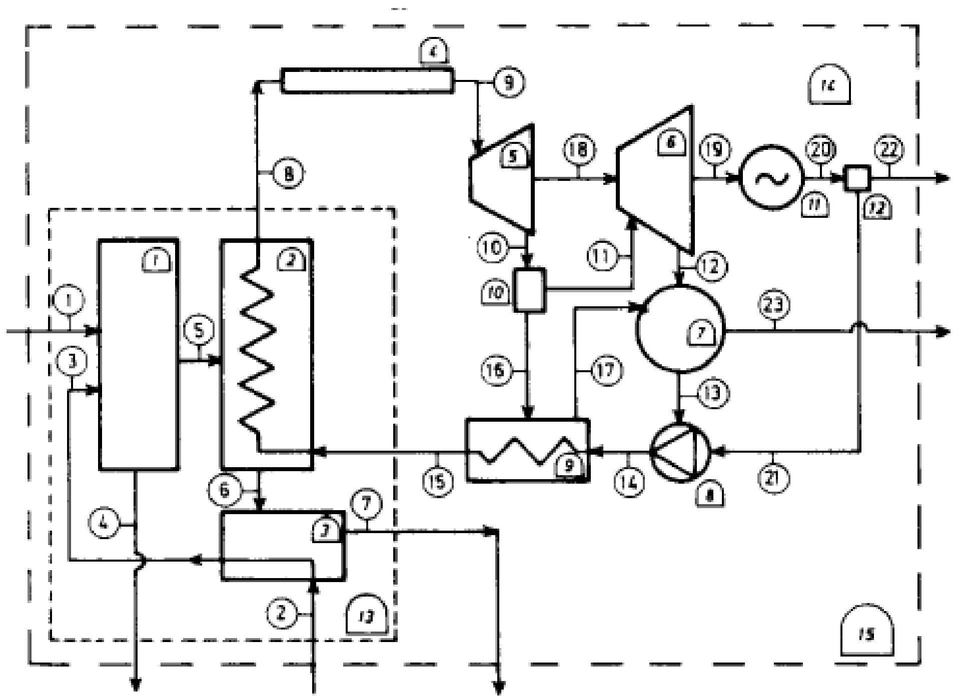
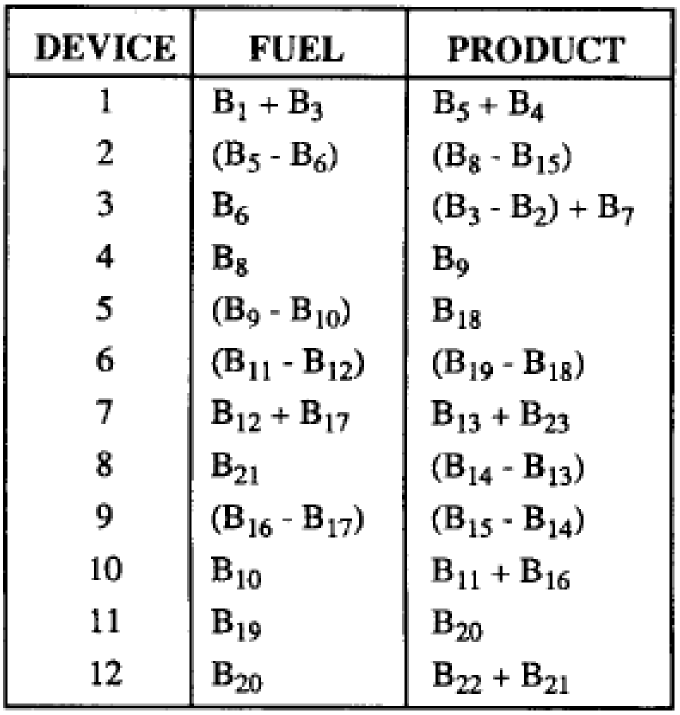


Figure 20 – Simple steam power plant[41]



DEVICE	FUEL	PRODUCT	
1	$B_1 + B_3$	$B_5 + B_4$	SG Combustion/Radiation
2	$(B_5 - B_6)$	$(B_8 - B_{15})$	SG convective
3	B_6	$(B_3 - B_2) + B_7$	Air Preheater
4	B_8	B_9	SG pressure loss
5	$(B_9 - B_{10})$	B_{18}	HP Turbine
6	$(B_{11} - B_{12})$	$(B_{19} - B_{18})$	LP Turbine
7	$B_{12} + B_{17}$	$B_{13} + B_{23}$	Condenser
8	B_{21}	$(B_{14} - B_{13})$	Pump
9	$(B_{16} - B_{17})$	$(B_{15} - B_{14})$	Feedwater Heater
10	B_{10}	$B_{11} + B_{16}$	Split
11	B_{19}	B_{20}	Electric Generator
12	B_{20}	$B_{22} + B_{21}$	Electric split

Fuel-Product definition table for steam power plant of Fig. 19

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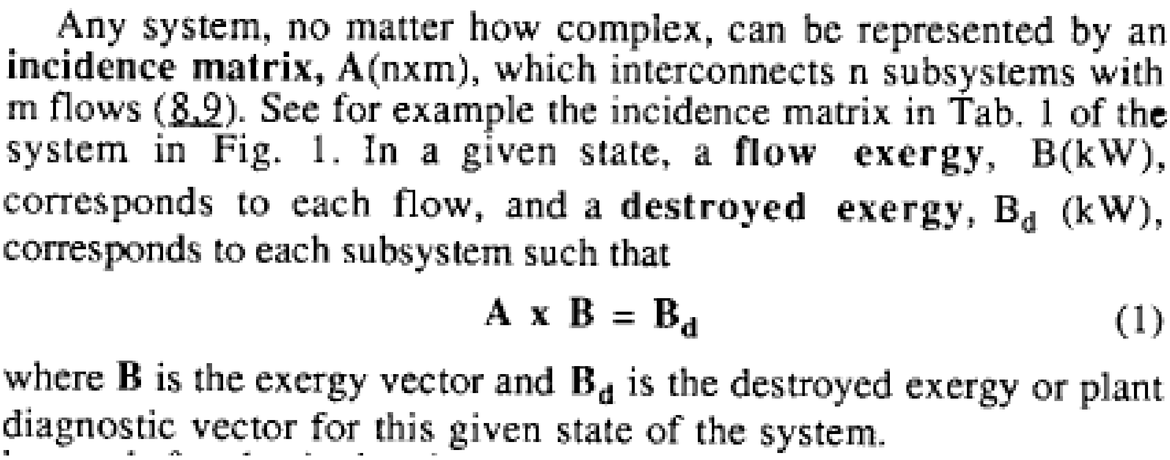
[41] Valero, A., Lozano, M., Munoz, M., A general theory of exergy saving. I: Exergetic cost, ASME AES division, 1986.



Any system, no matter how complex, can be represented by an **incidence matrix**, A(nxm), which interconnects n subsystems with m flows (8,9). See for example the incidence matrix in Tab. 1 of the system in Fig. 1. In a given state, a **flow exergy**, B(kW), corresponds to each flow, and a **destroyed exergy**, B_d (kW), corresponds to each subsystem such that

$$\mathbf{A} \times \mathbf{B} = \mathbf{B_d} \qquad (1)$$

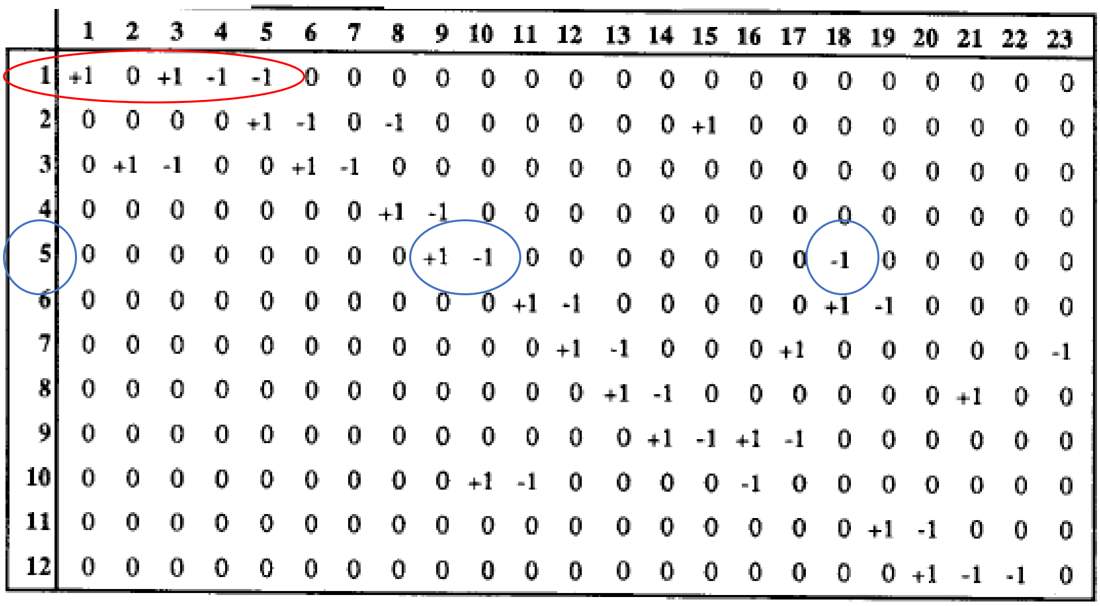
where **B** is the exergy vector and $\mathbf{B_d}$ is the destroyed exergy or plant diagnostic vector for this given state of the system.

SG Combustion/Radiation

Streams

Components

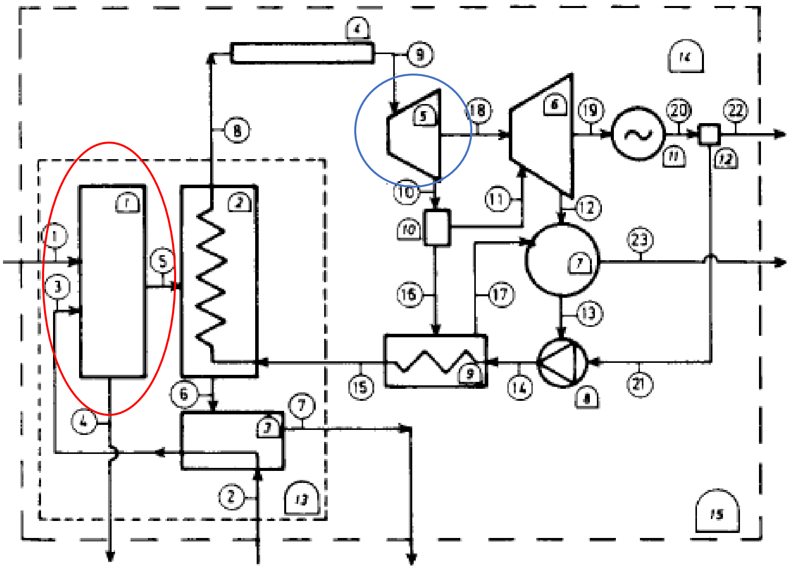
HP Turbine



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
1	+1	0	+1	-1	-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2	0	0	0	0	+1	-1	0	-1	0	0	0	0	0	0	+1	0	0	0	0	0	0	0	0
3	0	+1	-1	0	0	+1	-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0	+1	-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
5	0	0	0	0	0	0	0	0	+1	-1	0	0	0	0	0	0	0	-1	0	0	0	0	0
6	0	0	0	0	0	0	0	0	0	0	+1	-1	0	0	0	0	0	+1	-1	0	0	0	0
7	0	0	0	0	0	0	0	0	0	0	0	+1	-1	0	0	0	+1	0	0	0	0	0	-1
8	0	0	0	0	0	0	0	0	0	0	0	0	+1	-1	0	0	0	0	0	0	+1	0	0
9	0	0	0	0	0	0	0	0	0	0	0	0	0	+1	-1	+1	-1	0	0	0	0	0	0
10	0	0	0	0	0	0	0	0	0	+1	-1	0	0	0	0	-1	0	0	0	0	0	0	0
11	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	+1	-1	0	0	0
12	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	+1	-1	-1	0

Incidence Matrix (Components vs. flow streams) for Fig. 20 plant

+1 = input; -1 = output



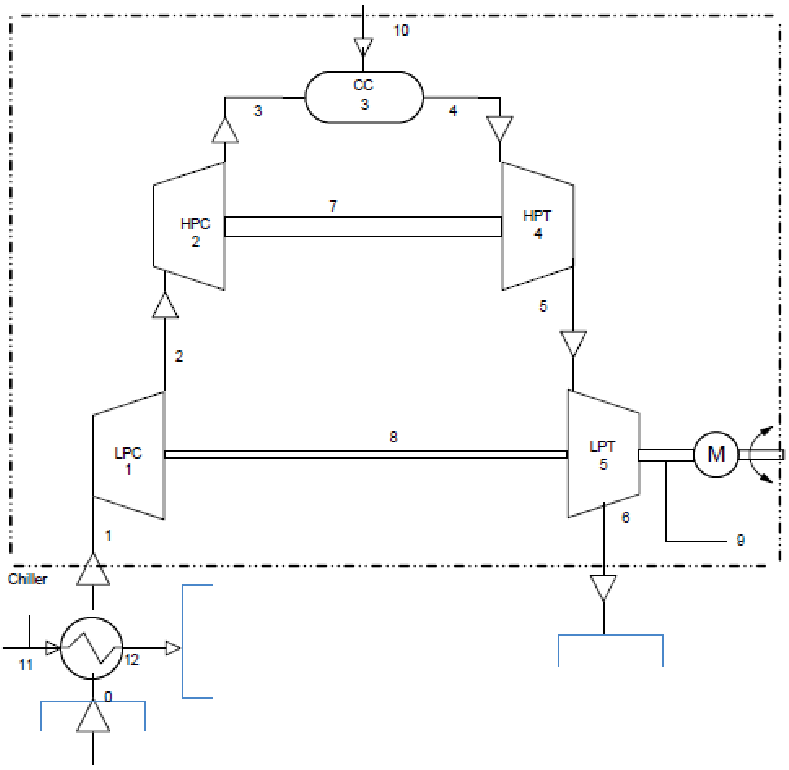


Figure 21 – Schematic of LM600 GT with chiller preconditioning[42]

Table 3. Incidence Matrix A of the LM-6000 system

	Subsystems/flow	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
LP Compressor	**1**	1	-1	0	0	0	0	0	1	0	0
HP Compressor	**2**	0	1	-1	0	0	0	1	0	0	0
Comb Chamber	**3**	0	0	1	-1	0	0	0	0	0	1
HP Turbine	**4**	0	0	0	1	-1	0	-1	0	0	0
LP Turbine	**5**	0	0	0	0	1	-1	0	-1	-1	0
	Perspective from the system	1	0	0	0	0	-1	0	0	-1	1

Table 4. Values of the exergetic flows, exergy loss, exergy destruction and exergetic efficiency of each subsystem of the LM-6000 system

Subsystem	**F (MW)**	**P (MW)**	**R (MW)**	**D (MW)**	**η**
LPC	11,99	8,71	0	3,28	0,73
HPC	46,84	45,1	0	1,73	0,96
CC	159	130,7	0	28,31	0,82
HPT	49,5	46,84	0	2,67	0,95
LPT	81,22	49,99	22,89	8,34	0,62

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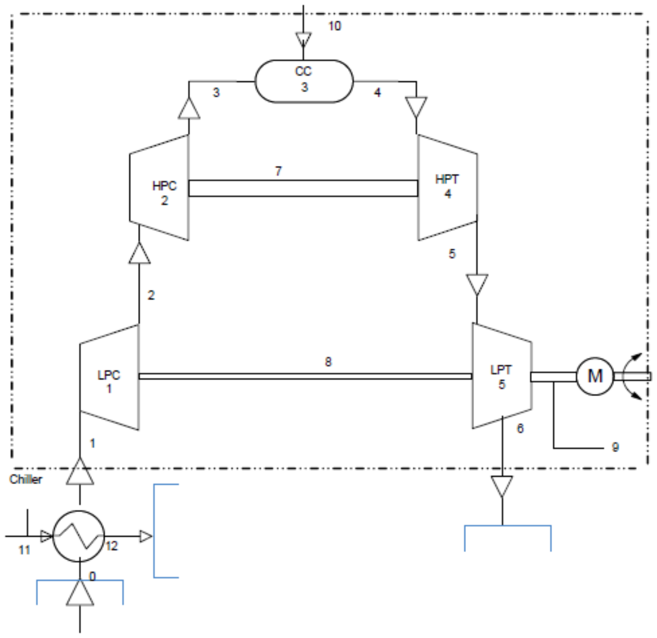
[42] Palma Rojas, S., Caldeira-Pires, A., Exergetic and Thermoeconomic Analysis of a Thermoelectric Power Plant Case Study: Thermoelectric Plant UTE - Rio Madeira, 2007 COBEM Conference, Brasilia.



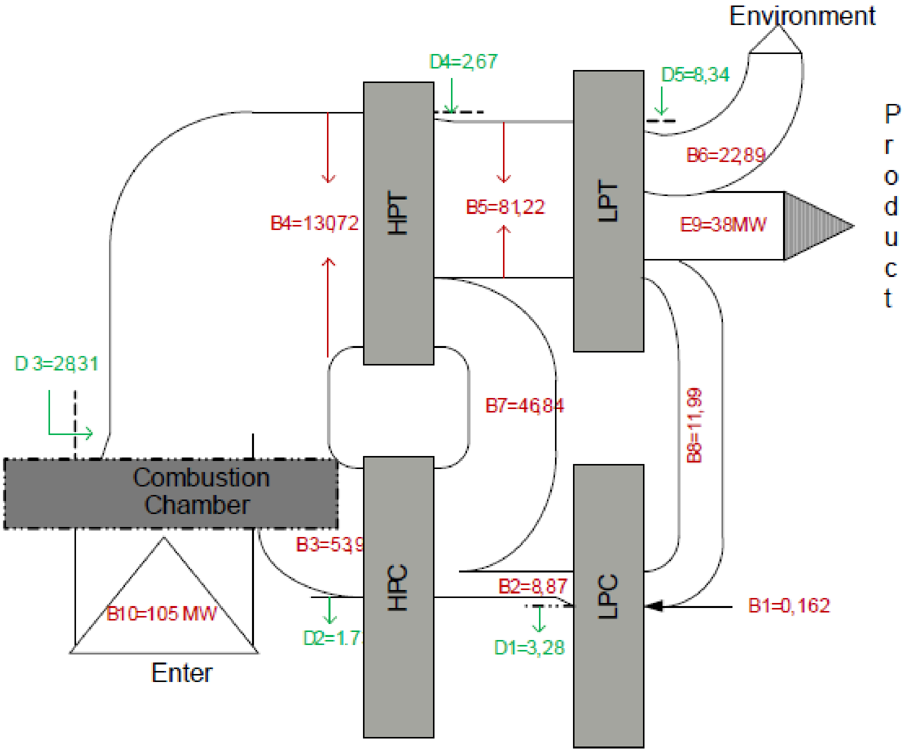


Figure 22 - Grassman Exergy diagram of LM 6000 GT

Physical and Chemical Exergy Splitting

A recommended step in Reactive systems is characterizing the component fuel and product streams separating Physical and Chemical Exergy.

For example, a combustion system is designed to transform Chemical Exergy (the most relevant part of the Fuel) into Physical Exergy (hot products stream at exit). In combustion systems, there is no chemical exergy in the products (combustion products).

When dealing with Chemical Reactors, there can be a chemical exergy product stream, which can be alone or coupled to a physical exergy product (often, the difference between the outlet and inlet exergy streams).

In some cases (e.g., fuel cells), a direct work (electricity) output can be obtained as a product. So in general, for chemical reactors there can be both physical and chemical fuel and product streams for the component.

The fuel/product accounting guidelines are not different from the general case, and as these course notes are not directed to a MSc or PhD Chemical Engineering course, no further details will be added concerning splitting of physical and chemical exergy.[43]

Combustion systems represent an exception, relevant also for Energy Engineers. In this case, however, it is sufficient to consider Chemical Exergy as a fuel for the combustor.

---

[43] Students interested in chemically-recuperated gas turbine cycles, or advanced composite cycles including devices such as SOFCs should apply splitting of chemical and physical exergy in the detailed system analysis.

Advanced Exergy Analysis

While the classical exergy analysis can be used to recognize the sources of inefficiency and irreversibilities, the Advanced Exergy Analysis (AEA) is aimed to identify the real potential for thermodynamic improvements of the system, introducing the splitting of exergy destruction into its avoidable and unavoidable parts.

In addition to that, for the AEA of complex energy systems, the exergy destruction of each component is analyzed not only from the isolated component point of view, but also extracting the contribution of the inefficiencies of the other components. This conceptual process splits the component exergy destruction into the endogenous and exogenous parts.

To facilitate the definition of endogenous and exogenous exergy destruction the following system, consisting of two components A and B, can be considered (Figure 22). To further simplify the presentation, it is assumed that there are no exergy losses. Thus all the exergy inefficiencies result from the exergy destruction within components A and B.

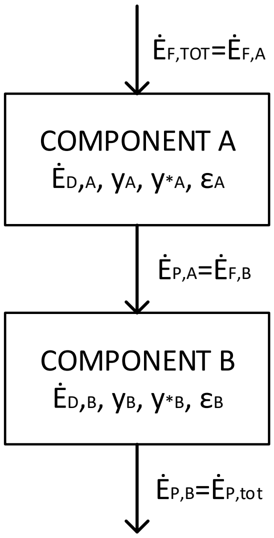


Figure 22: System in which the product of one component is the fuel of the next component.

The exergy destructions for the two components can be re-calculated tracing them back from the system output product stream[44]:

$$\dot{E}_{D,B} = \dot{E}_{P,tot}\left(\frac{1}{\varepsilon_B} - 1\right) \qquad (55)$$

$$\dot{E}_{D,A} = \frac{\dot{E}_{P,tot}}{\varepsilon_B}\left(\frac{1}{\varepsilon_A} - 1\right) \qquad (56)$$

Starting from th Product, the exergy destruction ratio of A and B can be expressed as a function of the exergy efficiency of each component, $\left(\frac{1}{\varepsilon} - 1\right)$.

Eq. 56 demonstrates that the rate of exergy destruction in component A depends not only on the component efficiency (ε_A), but also on the exergy efficiency of component B (ε_B).

Thus, the rates of exergy destruction should be used cautiously to characterize the performance of system components because, in general, a part of the exergy destruction occurring in a component is caused by the inefficiencies of the remaining system components (*exogenous exergy destruction*).

In AEA, the total component-related exergy destruction is treated as the sum of *exogenous* and *endogenous* exergy destructions.

---

[44] Actually any system should be analyzed making reference to the same product obtained; optimization means reduction of fuel consumption to obtain that product stream.

The endogenous term is the part of exergetic destruction due exclusively to the component being considered assuming that all remaining components operate with unit (100%) exergy efficiency.

Only in the component where $\dot{E}_{P,tot}$ is generated, the exogenous exergy destruction rate becomes zero[45].

The decomposition in avoidable and unavoidable exergy destruction is used to reveal the real potential for improvements, as it enables to recognize the exergy destruction that can be ralistically eliminated and to focus on it. The procedure is based on predefined real, unavoidable and theoretical operating conditions.

Real operating conditions are the ones currently achieved by the system.

Unavoidable operating conditions include the losses and the irreversibilities that cannot be realistically eliminated and imply a distinction between achievable and unachievable targets for future improvements.

Theoretical operating conditions are the ones that might be achieved in theory, but usually unlikely in practice, at least not in the near future.

Figure 23[46] is effective in representing the **UnavoidableExergy Destruction** (represented on the **X-axis**). Even augmenting the investment cost and improving the component quality, it is impossibile to achieve an Exergy Destruction from the component lower than the unavoidable limit (red vertical line).

---

[45] This is the last component in our example; but real systems may have products exiting the system boundaries at different components.

[46] Tsatsaronis, G., Park, MH, On avoidable and unavoidable exergy destructions and investment costs in thermal systems, Energy Conversion and Management, 43, 2002, 1259-1270

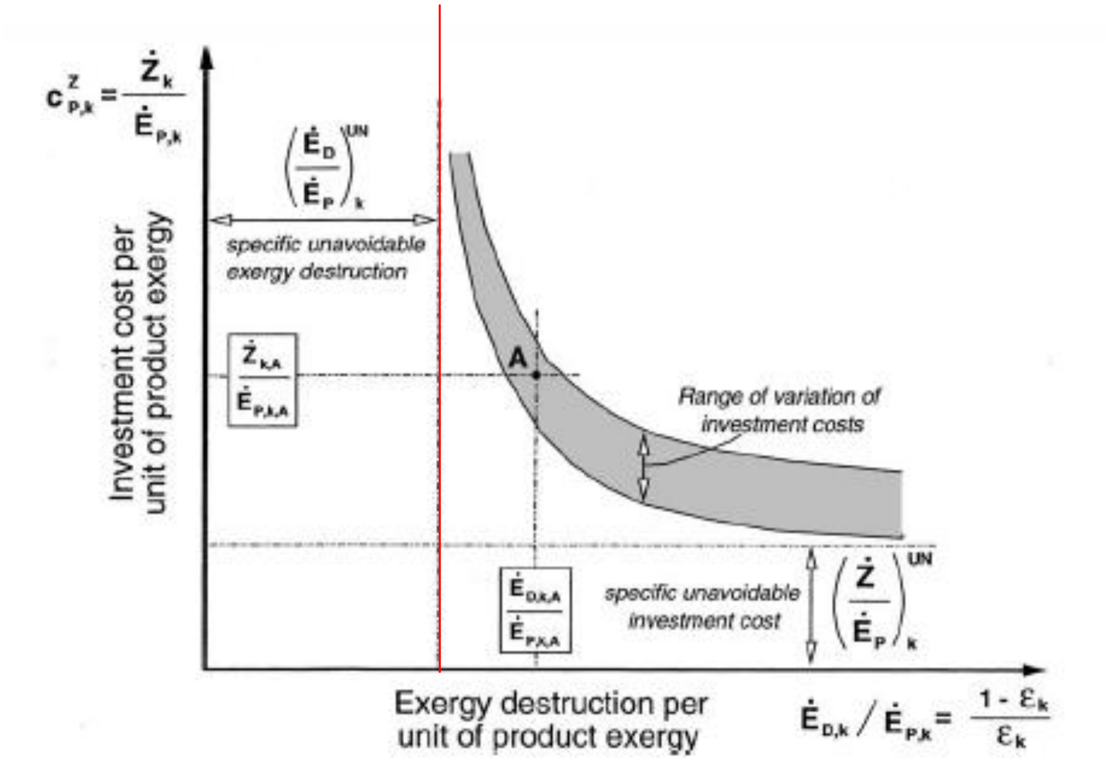


Figure 23 Exergy Destruction and Component cost. Unavoidable Exergy Destruction highlighted (red line).

The **X axis** represents the **Exergy Destruction**.

The **Y axis** represents the **Capital Cost of the Component**.

Both axes are made non-dimensional referring to the unit product exergy flow rate $\dot{E}_{Pk}$ [kW] = $\dot{m}_k e_k$

In principle, a component with better efficiency will be more expensive[47]. This is represented by the hyperbolic trend of the component cost versus exergy destruction.

---

[47] This is the link to Exergo-Economics. However, not all components in reality show this trend, which should be the normal one. There can be components where a cost reduction can be combined with a reduced exergy destruction. This represents clearly a recommended choice. In most other cases, the plant designer is called to make choices between an increased capital cost and a poorer thermodynamic performance (how much I am willing to pay to obtain top performance?).

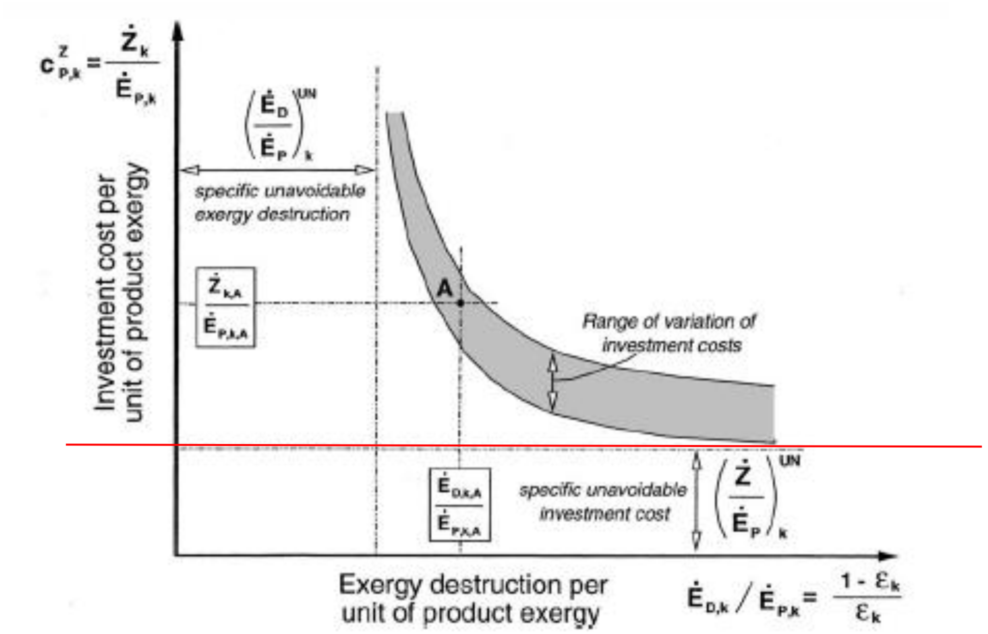


Figure 24 Exergy Destruction and Component cost. Lower limit of component cost highlighted (red line).

There is also a **lower limit to component cost** (unavoidable component cost: red horizontal line). This is the cost of a component having a very high (infinite) exergy destruction; however, the component cannot be eliminated as it is essential to operation of the system.

The **gray band** represents the Range of variation of investment costs. Different producers will be able to provide a component fulfilling the required duty at different costs; in general, a good component supplier will be able to apply advanced technologies (components having lower cost and better performance), which are typically represented by the lower curve. Components produced applying traditional, consolidated technologies are represented by the upper curve, and are not appealing on the market place (poor performance, higher cost).

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