

From the fuel heating values to the fuel exergy value in advanced energy systems

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Abstract:

Several advanced energy systems include less standard fuel oxidation conditions. This is particularly true when partial oxy-combustion, post-combustion of anodic gases of SOFC or CO₂ gas separation are considered. This paper reviews the theoretical basis for the determination of the heating values and of the exergy values of various fuels. As a reminder, the exergy value of fuels is developed using Gibbs free energies of formation and is illustrated with a van't Hoff box with compressors and turbines. The paper also discusses the molar exergy of diffusion which is important when assessing various CO₂ separation technologies as well as the relative importance of the reference environment. The concepts of fuel exergy for fuels and exergy of diffusion for inert species is clearly established. The choice of the value of the exergy of diffusion of liquid water is particularly sensitive when calculating the exergy value of hydrocarbon fuels in systems with gas condensation.

Keywords:

Thermodynamics; Fuel; Heating value; Exergy; Oxidation.

1. Introduction

In practice processes occurring within real energy system take place in a given surrounding environment (e.g. the atmosphere characterized by the pressure P_a , the ambient temperature T_a and its chemical composition). The latter is considered large enough for its main features like the pressure, the temperature and the mass concentrations to remain constant. Whatever resources are considered in energy systems their ultimate fate will end up to be in equilibrium with the environment.

Combustion gases from a fuel boiler will reach an equilibrium with the atmosphere after passing through the chimney exhaust. Energy and masses are conserved, but their potential to do work is ultimately degraded to be cancelled when the equilibrium with the atmosphere is reached, a thermodynamic state that is called the dead state. Therefore, every technical energy system, aim at exploiting at its best the potential of a resource from its original state to the ultimate state of the environment. For example, a fuel is interesting because its initial thermodynamic state is different from that of the one from the stable inert gasses of the atmosphere. The objective of the energy system designer is therefore to make the most of the chemical potential of the fuel for delivering energy services. The challenge lies on the manner that the fuel energy or the exergy potential can be coherently represented in the expressions of the Laws of thermodynamics.

Most publications like [2] apply the terminology of chemical exergy for fuels as well as for inert gases like molecular N₂. The objective of this paper is to reformulate a coherent and concise approach of the problem of the comparison between energy and exergy evaluation of fuels in modern energy systems. The paper advocates a clear differentiation between diffusion and reactive phenomena in the exergy analysis of fuel-based energy systems. It also expresses the interest of having a symmetry between energy and exergy approaches of fuels. In so doing the paper also highlights the importance of an existing model of reversible combustion for a proper understanding of the main concepts.

2. Combustion

Combustion is an oxidation process, air oxygen (O) being the dominant oxidizer used. The input mixture (M) is made of fuel and oxidizer, called "reactants" in chemistry, while the output combustion or oxidation gases (G) are the reaction "products", generally emitted directly to the atmosphere. When all fuel components are fully oxidized (reactants in *stoichiometric* proportions, see below) the combustion or oxidation is said to be complete and the reaction products are designated by G_c.

For simplicity of analysis, the most common fuels are often reduced to their main component only, i.e. natural gas to methane CH₄, gasoline to octane C₈H₁₈ and diesel fuel (or heating oil) to dodecane C₁₂H₂₆. More

generally, a generic molecule $C_aH_bO_cN_d$ can be used. The stoichiometric coefficients, stoichiometric air amount and volume ratio of the combustion products for such a generic molecule are given below. Note that for energy analyses a simple composition of air is assumed, with a molar fraction of O_2 of 0.21, the rest being essentially nitrogen with a molar fraction of 0.79.

2.1 Energy (heating value of fuel)

A convenient way to assess the energy that can be obtained from a fuel in basic energy analyses is the concept of "Heating Value, HV". Although there are several different heating value concepts that can be developed [1], heating and cooling systems are usually open systems, such as typical burners, and the combustion can be considered to take place at constant pressure (isobaric). Heating values are defined with respect to a given reference state (standard conditions) that is usually:

$$\text{Standard pressure } P^0 = 1 \text{ atm} = 1.01325 \text{ bar and standard temperature } T^0 = 25^\circ\text{C}$$

However, most fuels include hydrogen atoms that oxidize to give H_2O vapor in the combustion products. When cooling the combustion gases to recover their heat energy, this water vapor can condense - totally or partially - depending on its partial pressure in the gases P_v and the lowest temperature of the cooling medium. In fact, water vapor starts to condense as soon as its partial pressure corresponds to the saturation pressure P_v'' at what is called the **dew point**. In calorimeters, condensation takes place each time that the dew point temperature is higher than the standard temperature. This corresponds to:

$$\frac{P_v}{P} = \tilde{c}_{H_2O}^G \text{ with } P_v = P_v''(T) \text{ at the dew point} \quad (1)$$

In which $\tilde{c}_{H_2O}^G$ is the molar fraction of H_2O in the combustion gases.

The saturation pressure of water $P_v''(T)$ can be calculated on the basis of the following approximation of the Clausius-Clapeyron Eq. (2) [1]:

$$\ln\left(\frac{P_v''}{140974}\right) = \frac{-3928.5}{231.667+T} \quad (2)$$

Where P_v'' is in bar and T in degree Celsius. Equation valid for the temperature range from 0°C and 150°C .

2.1.1. Air factor and its influence on gas condensation

A minimum proportion of oxygen, called **stoichiometric**, is required to achieve a complete combustion of the fuel. When air is the oxidant source the ratio between the input air amount (A) and the stoichiometric amount (Ast) is the **air factor** λ defined by:

$$\lambda = \frac{N_A}{N_{Ast}} = \frac{M_A}{M_{Ast}} \quad (3)$$

Another parameter called **equivalence ratio** ϕ is also often used; it is defined by:

$$\phi = \frac{1}{\lambda} \quad (4)$$

Note that the quantity of air corresponding to the stoichiometric quantity of oxygen is also called **theoretical air** [2].

Another ratio commonly used is the air-fuel ratio that is the ratio between the amount of air and the amount of fuel in mass (AF) or molar ($\tilde{A}\tilde{F}$) units. The conversion between the mass and the molar air-fuel ratios corresponds to:

$$AF = \tilde{A}\tilde{F} \frac{\tilde{m}_A}{\tilde{m}_F} \quad (5)$$

2.1.2. Isobaric heating values

Heating values are typically measured in calorimeter at constant volume or at constant pressure [1]. In order to simplify the discussion in this paper and since the majority of oxidation-based energy systems are open systems in quasi-steady operation this paper focusses on constant pressure (isobaric conditions).

For hydrocarbons the dew point is higher if the hydrogen/carbon ratio is higher and lower if the degree of dilution of water vapor is high in combustion gases (high air factor λ). This is the reason why there is a need to introduce two different isobaric heating values:

- **higher heating value HHV** when all H_2O formed during combustion is condensed;
- **lower heating value LHV** when none of H_2O formed during combustion is condensed

Those are defined by the following equations:

$$\text{Specific isobaric Heating Value. HHV (or LHV)} = \Delta h^0 = \frac{H_M^0 - H_{Gc}^0}{M_F} \left[\frac{J}{kgF} \right] \quad (6)$$

$$\text{Molar isobaric Heating Value. HHVm (or LHVm)} = \Delta \tilde{h}^0 = \frac{H_M^0 - H_{Gc}^0}{N_F} \left[\frac{J}{kmolF} \right] \quad (7)$$

The exponent $()^0$ reminds that those values are determined at a given reference state and H_{Gc}^0 varies depending on whether there is full or no condensation of the formed vapor from hydrogen. The following relation links the higher and lower heating values:

$$HHV = LHV + \dot{M}_{H_2O_p} q_{vap}^0 / \dot{M}_F \quad (8)$$

In which:

- $\dot{M}_{H_2O_p}$ is the total mass flow of H_2O produced during combustion,
- q_{vap}^0 is the latent heat of H_2O at the standard temperature.

The heating values of most common fuels can be found in the literature with specific or molar values.

The energy balance with all terms numerically positive can be expressed by:

$$\sum_k \dot{E}_k^+ + \sum_i \dot{Q}_i^+ + \dot{Y}_{comb}^+ + \sum_n \dot{Y}_n^+ - \dot{Q}_a^- = \sum_k \dot{E}_k^- + \sum_i \dot{Q}_i^- + \sum_n \dot{Y}_n^- \quad (9)$$

Considering separately the network denominated with the subscript $()_{comb}$ in which combustion takes place:

$$\dot{Y}_{comb}^+ = \dot{M}_F (HHV + \hat{h}_F) + \dot{M}_A \hat{h}_A - \dot{M}_G \hat{h}_G - \sum (\dot{M}_I HHV_I) - (\dot{M}_{H_2O_p} - \dot{M}_{cond}) q_{vap}^0 \quad (10)$$

Where:

- $\hat{h}_F = \int_{T^0}^{T^F} dh_F$ (11) and $\hat{h}_A = \int_{T^0}^{T^A} dh_A$ (12) and $\hat{h}_G = \int_{T^0}^{T^G} dh_G$ (13) are accounting for the fact that the entering reactants and exiting products in practice have a temperature different from that of the reference standard state,
- \dot{M}_I and HHV_I are the mass-flows of unburned hydrocarbons and their higher heating value, in the case of incomplete combustion,
- $\dot{M}_{H_2O_p}$ is the total mass-flow of H_2O produced during combustion,
- \dot{M}_{cond} is the mass-flow of H_2O effectively condensed.

Figure 1 illustrates the heat gains that can be obtained by condensing the combustion gases in a condensing boiler for various fuels. The same applies to the exhaust gases of cogeneration units (engines or gas fed fuel cells) and gas fired heat pumps. The more diluted the resulting water vapor is (high λ), the less heat can be recovered from condensation and the lower is the dew point temperature. The higher the H/C ratio, the higher the dew point temperature. We can see, for example, that stoichiometric gas engines ($\lambda = 1$) allow to potentially recover more condensation heat and at a higher temperature than lean burn gas engines ($\lambda \cong 1.6$).

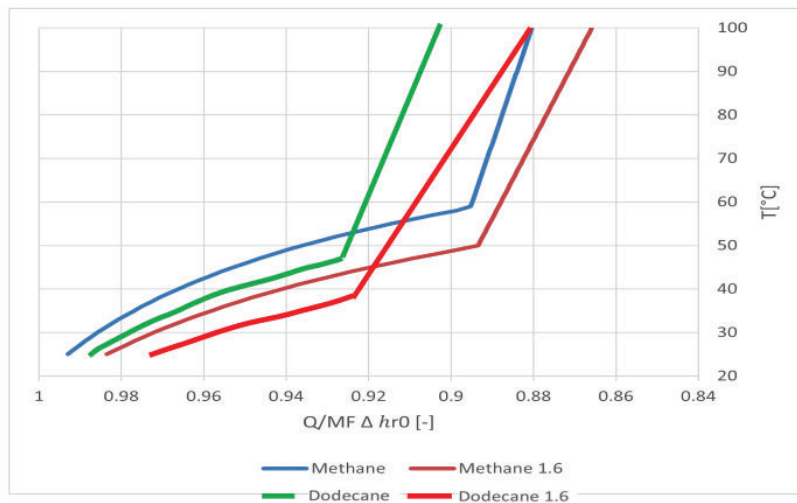


Figure 1. Parts of the higher heating value recoverable when cooling the combustion gases from a condensing boiler down to 25°C with $\lambda = 1$ (blue & green) or 1.6 (red & brown) for methane CH_4 (close to natural gas) and $C_{12}H_{26}$ (close to fuel oil). Here Q is the heat rate obtained, MF is the mass flow rate of fuel and Δhr_0 is the isobaric higher heating value.

2.1.3. Enthalpies of formation and absolute entropies

In processes that do not involve chemical reactions, no species is modified and therefore all are considered inert, thus the reference of each of their thermodynamic state properties cancels out between inlet et outlet in energy or exergy balances. This is not the case anymore when reactions take place and new species are formed. In such conditions it becomes important to define coherent references. Hence the use of the definition of **standard enthalpies of formation**, given per molar units in thermodynamic tables. Since entropy is also

essential in the Second Law and exergy analyses, the use of **absolute entropies** for all species is also of prime importance.

The values of enthalpies of formation of species that can be considered stable in the environment are arbitrarily assigned a zero value at the standard state. When this is not the case, they are determined either from calorimetric experiments or based on methods of statistical thermodynamics using spectroscopic measures. The fact that the reactions are exo- or endo-thermic influences the sign of the enthalpies of formation. For example, the reaction $2H_2 + O_2 \rightarrow 2H_2O$ is exothermic, which implies that heat needs to be extracted to come down to the standard temperature after reaction. Therefore, the enthalpy of formation of H_2O is negative, which is coherent with the convention of "positive entering" in a calorimeter for example.

The isobaric molar $\Delta\tilde{h}^0$ and specific heating value Δh^0 can then be determined by the following generic equations:

$$\Delta\tilde{h}^0 = \sum_i \left[\frac{N_i \tilde{h}_{fi}^0}{N_F} \right] - \sum_j \left[\frac{N_j \tilde{h}_{fj}^0}{N_F} \right] \quad \left[\frac{J}{kmol_F} \right] \quad (14)$$

$$HHV = \Delta h^0 = \sum_i \left[\frac{N_i \tilde{h}_{fi}^0}{M_F} \right] - \sum_j \left[\frac{N_j \tilde{h}_{fj}^0}{M_F} \right] \quad \left[\frac{J}{kg_F} \right] \quad (15)$$

In which all the H_2O formed during combustion is condensed and, as before:

- subscript i refers to all compounds of the reactants (fuel and air)
- subscript j refers to all compounds of the reaction products (combustion gases)

3. Exergy value and exergy of diffusion (also called chemical exergy)

The **advantage of the heating values based on the First Law of thermodynamics is that they are independent from the presence of inert gases as long as enough oxygen is provided to allow for a complete combustion**. As such they do not account for the level of purity of the oxygen (pure or mixed with air) or for the concentration of CO_2 in the combustion gases. These parameters however play an increasing role in all energy systems that include CO_2 separation or oxy-combustion for example. Then the Second Law starts to be of primary importance and exergy analyses can provide a more coherent framework to evaluate advanced systems.

3.1 Convention regarding the exergy value

The objective is not only to consider thermomechanical equilibrium with the environment (P^0, T^0) (thermo-mechanical dead state) but also physico-chemical equilibrium (P^{00}, T^0, s^{00}) (dead states of each species). Hence, the need to precise a more complete reference of the environment considered, as described in Table 1.

Table 1. Partial pressure and molar fractions of the main gaseous constituents of the standard atmosphere (at the standard conditions with $P^0 = 1.01325 \text{ bar}$ and $T^0 = 25^\circ\text{C}$)

Substance	P_i [bar]	\tilde{c}_i^A [$kmol_i/kmol_A$]
N_2	0.7665	0.7565
O_2	0.2056	0.2030
Ar	0.0091	0.0090
$H_2O(g)$	0.0316	0.0312
CO_2	0.0003	0.0003

One further component to account for is liquid water resulting for example from condensation of combustion gases. It will be discussed later.

Furthermore, a convention is established to clarify the following conditions for the evaluation of the exergy value resulting from reactive processes:

- The fuel F and the air A enter separately (no premixing with the fuel)
- Each constituent of the reaction products Gc (combustion gases) ends up physically mixed with the standard atmosphere, i.e. at its partial pressure P_i^{00}
- Water exists in the final combustion products Gc either in liquid or vapor form at the limit of saturation, i.e. at the partial pressure of saturation in the standard atmosphere.

These conditions being set, the corresponding values for the **exergy value of a fuel** are the following:

$$\overline{EXV} = \Delta\tilde{k}^0 = \sum_i \left[\frac{N_i \tilde{k}_{fi}^{00}}{N_F} \right] - \sum_j \left[\frac{N_j \tilde{k}_{fj}^{00}}{N_F} \right] \quad \left[\frac{J}{kmol_F} \right] \quad (16)$$

$$EXV = \Delta k^0 = \sum_i \left[\frac{N_i \tilde{k}_{fi}^{00}}{M_F} \right] - \sum_j \left[\frac{N_j \tilde{k}_{fj}^{00}}{M_F} \right] \quad \left[\frac{J}{kg_F} \right] \quad (17)$$

In accordance with the basic definition of exergy, the specific exergy value Δk^0 corresponds to the maximum work e_{max}^F that can be recovered from a fuel in an open reversible combustion in steady state, like in Figure 2. In principle, we should also consider whether or not there is condensation of the water formed during combustion. However as shown in [1] the difference between a higher and a lower exergy value is negligible, in particular when $T_a = T^0$. This is logical since the Carnot factor $(1 - T_a/T^0)$ is zero. Hence **the advantage of the exergy analysis of systems including oxidation processes is that a single exergy value can be considered in first approximation for fuels.**

Table 2. Features of the main species involved in combustion [5]

Species	Symbol	State	Molar mass [kg/kmol]	Enthalpy of formation [kJ/kmol]	Absolute entropy [kJ/(kmol K)]	Standard free enthalpy* [kJ/kmol]	Exergy value or Exergy of diffusion
Graphite	C	Solid	12.01	0	5.6944	0	410545
Molecular hydrogen	H ₂	Gas	2.02	0	130.586824	0	235210
Molecular nitrogen	N ₂	Gas	28.01	0	191.50168	0	691.066
Molecular oxygen	O ₂	Gas	32	0	205.028552	0	3946.5
Carbon monoxide	CO	Gas	28.01	-110541	197.9032	-137277	275241
Carbon dioxide	CO ₂	Gas	44.01	-393505	213.67688	-394383.8	20107.5
Water liq.	H ₂ O	Liquid	18.02	-285830	69.91464	-237178.4	5.10164
Water vap.	H ₂ O	Gas	18.02	-241818	188.715136	-228588.6	8594.9
Methane	CH ₄	Gas	16.04	-74851.76	186.27168	-50835.6	830130
Ethane	C ₂ H ₆	Gas	30.07	-84684.16	229.11584	-32802.6	1493918
Propane	C ₃ H ₈	Gas	44.1	-103846.9	270.20272	-23555.9	2148920
n-butane	n-C ₄ H ₁₀	Gas	58.12	-126147.6	310.11808	-17.1544	2818213
Heptane	C ₇ H ₁₆	Liquid	100.2	-224387.9	326.01728	1757.28	4757253
n-octane	C ₈ H ₁₆	Gas	114.2	-208446.9	466.7252	16401.28	5417652
n-octane	C ₈ H ₁₆	Liquid	114.2	-249952.2	357.732	7405.68	5408656
dodecane	C ₁₂ H ₂₆	Liquid	170.33	-352100	490.66	50160	8034431
Methanol	CH ₃ OH	Gas	32.04	-201083	239.70136	-162422.9	720516
Methanol	CH ₃ OH	Liquid	32.04	-239031.9	127.23544	-166816.1	716122
Ethanol	C ₂ H ₅ OH	Gas	46.07	-234429.5	282.58736	-167903.9	1360790
Ethanol	C ₂ H ₅ OH	Liquid	46.07	-276980.8	161.04216	-174179.92	1354514
Ammonia	NH ₃	Gas	17.03	-46107.7	192.33848	-16484.96	336676

*also called Gibbs function of formation or Gibbs free energy of formation

Table 2 provides the molar masses \tilde{m} , the enthalpies of formation \tilde{h}_f^0 , the absolute entropies \tilde{s}^0 , the standard free enthalpies \tilde{g}_f^0 , the exergy values $\overline{EXV} (= \Delta \tilde{k}^0)$, resp. the exergies of diffusion \tilde{e}_d^0 of a number of compounds considered in practice. For reference, the calculator [12] provides slightly different values with a fairly high value for the entropy of diffusion of H₂O liquid, reason why we kept here the original values of [5].

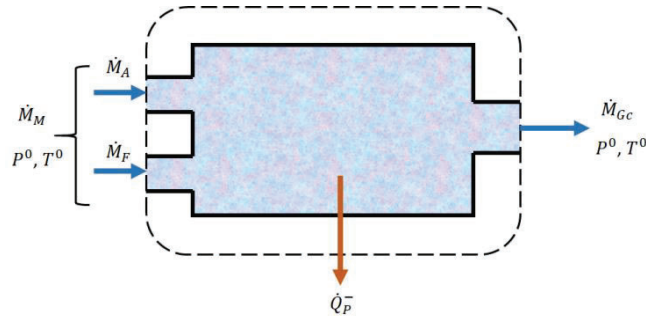


Figure 2. Example of combustion in steady-state operation at constant pressure

3.2 Model of reversible combustion or oxidation

According to the definition of exergy the maximum work to be considered is the ideal work that could be recovered from reversible processes. In this context the idea of a **reversible combustion** is not obvious but can be explained with the use of a so-called van't Hoff box (cited in [3]) with compressors and turbines and semi-permeable membranes (Figure 3). Semi-permeable membranes are membranes that let only one species go through when the partial pressure of that species is not balanced on both sides of the membrane. One practical example of semi-permeable membrane is the solid electrolyte of a Solid Oxide Fuel Cell (ionic conductor) that, in certain conditions of temperatures, let only oxygen go through. The principle of a van't Hoff box is that the species inside the box are near the chemical equilibrium when reactions occur in the direction of the arrows shown in Figure 3, but the process can be reversed with only a slight change in the pressure between inlet and outlet with in this case arrows being reversed. For example, the species i_2 in Figure 3 could be oxygen taken from the atmosphere and i_1 a gaseous fuel like CH_4 . Then j_2 could be CO_2 and j_1 would be H_2O according to the well-known reaction:

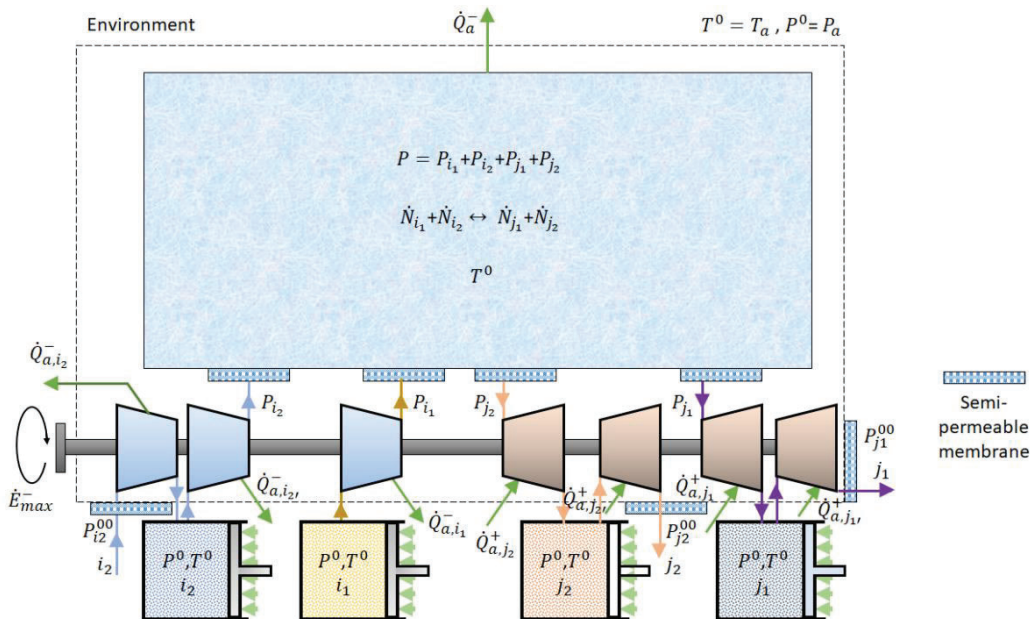


Figure 3. Schematic representation of the reversible combustion of a fuel

The double arrow in the above equation indicates that the reaction is reversible close to equilibrium. Mechanically the first compressor is used to suck O_2 from its partial pressure $P_{i_2}^{00}$ in the atmosphere to a dedicated storage at pressure P^0 , and the second compressor is pushing O_2 into the box at pressure P . The third compressor is pushing CH_4 from pressure P^0 to pressure P in the box. Then, on the same shaft one could imagine 4 turbines, 2 for CO_2 and 2 for H_2O , all gases ending up at their partial pressure in the atmosphere. All these machines are supposed to be isothermal, exchanging heat only with the atmosphere. Reversing the processes would mean that the turbines become compressors and the compressors become turbines. The net

mechanical power \dot{E}_{max}^- that can be obtained from the process corresponds to an exergy rate equal to the specific exergy value of the fuel multiplied by the mass flow of fuel.

Through this representation one sees that if the oxidant is pure oxygen, more work can be obtained since the work required by the first compressor is not needed. On the other end if the concentrated CO₂ or H₂O exiting the system are just mixed with the atmosphere, then an opportunity to recover more work is lost. It is interesting to note that the theoretical work delivered by the second CO₂ turbine is equivalent to the minimum amount of work required to separate the same amount of CO₂ from the atmosphere for separate storage.

Let us first calculate the work recovered in steady-state operation for the simple case without the first compressor and the two turbines adapting the state of the exhaust gases to the atmospheric conditions:

$$\dot{E}^- = \dot{Q}_a^+ + \sum_i [\dot{M}_i h_{fi}^0] - \sum_j [\dot{M}_j h_{fj}^0] \quad (19)$$

Assuming that the processes are reversible, then the Second Law gives:

$$\dot{Q}_a^+ = T^0 (\sum_j [\dot{M}_j s_j^0] - \sum_i [\dot{M}_i s_i^0]) \quad (20)$$

Therefore:

$$\dot{E}^- = \dot{E}_{max}^- = \sum_i [\dot{M}_i (h_{fi}^0 - T^0 s_i^0)] - \sum_j [\dot{M}_j (h_{fj}^0 - T^0 s_j^0)] \quad (21)$$

$$\dot{E}^- = \dot{E}_{max}^- = \sum_i [\dot{M}_i g_{fi}^0] - \sum_j [\dot{M}_j g_{fj}^0] \quad (22)$$

Where g_f^0 is the Gibbs free energy (also called free enthalpy) of formation.

For ideal gases the reversible mechanical power of an isothermal compressor is known to be:

$$\dot{E}^+ = \dot{N} \int_{P_{in}}^{P_{out}} \tilde{v} dP = \dot{N} \int_{P_{in}}^{P_{out}} \tilde{r} T^0 \frac{dP}{P} = \dot{N} \tilde{r} T^0 \ln \left(\frac{P_{out}}{P_{in}} \right) \quad (23)$$

Where \tilde{r} is the molar universal gas constant and the species behave like an ideal gas.

Inverting the integral limits give the equivalent equation for turbine.

Therefore, the net maximum work of the case of Figure 3 corresponds to:

$$\dot{E}_{max}^- = \sum_i [\dot{N}_i \tilde{g}_{fi}^0] - \sum_j [\dot{N}_j \tilde{g}_{fj}^0] + \dot{N}_{j1} \tilde{r} T^0 \ln \left(\frac{P^0}{P_{j1}^0} \right) + \dot{N}_{j2} \tilde{r} T^0 \ln \left(\frac{P^0}{P_{j2}^0} \right) - \dot{N}_{i2} \tilde{r} T^0 \ln \left(\frac{P^0}{P_{i2}^0} \right) \quad (24)$$

Let us also introduce the **molar exergy of diffusion** \tilde{e}_{dk}^0 for a species k:

$$\tilde{e}_{dk}^0 = \frac{\dot{N}_k}{\dot{N}_F} \tilde{r} T^0 \ln \left(\frac{P^0}{P_{k0}^0} \right) \quad (25)$$

The ratio $\frac{\dot{N}_k}{\dot{N}_F} = \nu_k$ is called stoichiometric coefficient and the **molar exergy value of a fuel** can be written in the following compact form:

$$\frac{\dot{E}_{max}^-}{\dot{N}_F} = \Delta \tilde{k}^0 = \sum_i [\nu_i \tilde{g}_{fi}^0] - \sum_j [\nu_j \tilde{g}_{fj}^0] + \sum_j [\tilde{e}_{dj}^0] - \sum_i [\tilde{e}_{di}^0] \quad (26)$$

$$\overline{EXV} = \Delta \tilde{k}^0 = \Delta \tilde{g}_f^0 + \sum_j [\tilde{e}_{dj}^0] - \sum_i [\tilde{e}_{di}^0] \quad (27)$$

The absolute free enthalpy \tilde{g}_f^0 can be calculated from the absolute enthalpies and the absolute entropies according to the following relation:

$$\tilde{g}_f^0 = \Delta \tilde{h}_f^0 - T^0 \sum (\tilde{s}_p^0 - \tilde{s}_R^0) \quad (28)$$

Note that in the literature [4], [2] all terms of the equation (3.114) are called **standard chemical exergies** although they refer to chemically stable substances and their exergy potential only lies in their partial pressure relative to the environment. Hence our terminology of **exergy value** $\overline{EXV} = \Delta \tilde{k}^0$ of the fuels and **exergy of diffusion** for the other terms like the oxidants (i.e. O₂) or the stable combustion products like CO₂ or H₂O(g). In that way the symmetry between the heating values of fuels and their exergy value is kept, since the expression "heating value" is not to be used for inert components.

We also have the relation [2]:

$$\tilde{s}_i^{00}(T, P_i) = \tilde{s}_i^0(T) - \tilde{r} \ln \left(\frac{P_i}{P^0} \right) = \tilde{s}_i^0(T) - \tilde{r} \ln \left(\frac{\tilde{c}_i^A P}{P^0} \right) \quad (29)$$

Note that, in practice, real fuels are often mixtures of monomolecular fuels. Natural gas being the most common example. Since mixing implies diffusion losses, the exergy value of such a real fuel cannot be the simple addition of the relative exergy values of the n fuel components but corresponds to:

$$\Delta \tilde{k}^0 = \sum_1^n \tilde{c}_i \Delta \tilde{k}_i^0 + \tilde{r} T_a \sum_1^n \tilde{c}_i \ln \tilde{c}_i \quad (30)$$

3.3 Exergy values of more complex technical fuels

However, the exergy value of most solid or liquid technical fuels, which are complex mixtures of chemical compounds, is often difficult to determine. Various evaluations have been made on the basis of statistical

methods [4] using the concentration of basic components in the fuel like C, H, O, N and S as well as their LHV or HHV.

Table 3. Energy (heating) and exergy values of common fuels at the standard conditions of 1 atm and 25°C [5]

Fuel	State	LHV = Δh_i^0 [kJ/kg]	HHV = Δh_s^0 [kJ/kg]	$\overline{LHV} = \Delta \tilde{h}_i^0$ [kJ/kmol]	$\overline{HHV} = \Delta \tilde{h}_s^0$ [kJ/kmol]	EXV = Δk^0 [kJ/kg]	$\overline{EXV} = \Delta \tilde{k}^0$ [kJ/kmol]
C	Solid	32765	32765	393510	393510	34183	410545
CO	Gas	10103	10103	282980	282980	9831	275241
H ₂	Gas	119716	141500	241826	285830	116441	235210
S	Solid	9250	9250	296600	296600	19011	609600
CH ₄	Gas	50018	55505	802292	890300	51757	830130
C ₂ H ₆	Gas	47512	51903	1428698	1560710	49678	1493418
C ₇ H ₁₆	Liquid	44559	48072	4464778	4816810	47460	4757253
C ₂ H ₆	Gas	47512	51903	1428698	1560710	49678	1493418
C ₈ H ₁₈	Liquid	44788	48255	5116144	5512150	47435	5408656
C ₁₂ H ₂₆	liquid	44574	47838	7592289	8148246	47169	8034431
CH ₃ OH	Gas	21110	23850	676364	764154	22544	720516
CH ₃ OH	Liquid	19936	22683	638762	726770	22367	716122
C ₂ H ₅ OH	Gas	27720	30590	1277060	1409281	29605	1360790
C ₂ H ₅ OH	Liquid	26818	29683	1235498	1367510	29386	1354514

However, a simplified approach to evaluate the chemical exergy of common combustible raw materials has been also proposed by [4].

$$\Delta k^0 = \alpha(LHV) \quad \text{or} \quad \Delta k^0 = \beta(HHV) \quad (31)$$

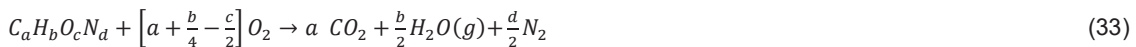
Table 4. Coefficients to evaluate the exergy value of fuels [4]

Fuel	Coefficient	
	α	β
Wood	1.15	1.05
Fuel oil	1.07	0.99
Natural gas (high methane)	1.04	0.99
Hard coal	1.09	1.03
Coke	1.06	1.04
Lignite	1.17	1.04
Coke-oven gas	1	0.89
Blast furnace gas	0.98	0.97

The following more detailed approach is also proposed for wood by [4].

$$\beta = \frac{1.0412 + 0.2160 \left(\frac{c_{H_2}^F}{c_C^F} \right) - 0.2499 \left(\frac{c_{O_2}^F}{c_C^F} \right) \left[1 + 0.7884 \left(\frac{c_{H_2}^F}{c_C^F} \right) \right] + 0.0450 \left(\frac{c_{N_2}^F}{c_C^F} \right)}{1 - 0.3035 \left(\frac{c_{O_2}^F}{c_C^F} \right)} \quad \text{valid for } \frac{c_{O_2}^F}{c_C^F} \leq 2.67 \quad (32)$$

3.4 Exergy balance for a generic fuel molecule $C_a H_b O_c N_d$



$$\frac{\dot{E}^-}{\dot{N}_F} = \frac{\dot{Q}^+}{\dot{N}_F} + \tilde{h}_F^0 + \left[a + \frac{b}{4} - \frac{c}{2} \right] \tilde{h}_{O_2}^0 - a \tilde{h}_{CO_2}^0 - \frac{b}{2} \tilde{h}_{H_2O}^0 - \frac{d}{2} \tilde{h}_{N_2}^0 \quad (34)$$

Second Law for steady-state operation:

$$0 = \frac{\dot{Q}^+}{\dot{N}_F T^0} + \tilde{s}_F^{00} + \left[a + \frac{b}{4} - \frac{c}{2} \right] \tilde{s}_{O_2}^{00} - a \tilde{s}_{CO_2}^{00} - \frac{b}{2} \tilde{s}_{H_2O}^{00} - \frac{d}{2} \tilde{s}_{N_2}^{00} + \frac{\dot{S}^i}{\dot{N}_F} \quad (35)$$

By substituting the value $\frac{\dot{Q}^+}{\dot{N}_F}$ in Equation (34) one gets:

$$\frac{\dot{E}^-}{\dot{N}_F} = \tilde{h}_F^0 + \left(a + \frac{b}{4} - \frac{c}{2} \right) \tilde{h}_{O_2}^0 - a \tilde{h}_{CO_2}^0 - \frac{b}{2} \tilde{h}_{H_2O}^0 - \frac{d}{2} \tilde{h}_{N_2}^0 - T^0 \left[\tilde{s}_F^{00} + \left(a + \frac{b}{4} - \frac{c}{2} \right) \tilde{s}_{O_2}^{00} - a \tilde{s}_{CO_2}^{00} - \frac{b}{2} \tilde{s}_{H_2O}^{00} - \frac{d}{2} \tilde{s}_{N_2}^{00} \right] - T^0 \frac{\dot{S}^i}{\dot{N}_F} \quad (36)$$

The transition of the absolute entropy from the thermomechanical dead state to the global dead state is given by Equ.(34).

For a generic molecule, Equ. (36) can also be written as:

$$\Delta \bar{k}^0 \text{ (or } \bar{e}_d^0) = \left[\tilde{g}_{f C_a H_b O_c N_d}^0 + \left(a + \frac{b}{4} - \frac{c}{2} \right) \tilde{g}_{f O_2}^0 - a \tilde{g}_{f CO_2}^0 - \frac{b}{2} \tilde{g}_{f H_2O}^0 - \frac{d}{2} \tilde{g}_{f N_2}^0 \right] + \tilde{r} T^0 \ln \left[\frac{\left(\bar{c}_{O_2}^A \right)^{\left(a + \frac{b}{4} - \frac{c}{2} \right)}}{\left(\bar{c}_{CO_2}^A \right)^a \left(\bar{c}_{H_2O}^A \right)^{\frac{b}{2}} \left(\bar{c}_{N_2}^A \right)^{\frac{d}{2}}} \right] \quad (37)$$

All data from species involved in combustion (Table 2), either exergy values for fuels or exergies of diffusion for inert species can typically be generated by Eq. (37).

3.5 Liquid water as a special case

Table 1 provides the values for a standard gaseous environment. We all know, however, that the environment consists of various equilibria like the equilibrium between surface water and the local gaseous atmosphere that usually shows a temperature difference. When dealing in particular with heating and cooling services, but also with power plants, the gaseous atmosphere is the most important environment since heat losses or gains as well as oxidant input and gas exhausts take place with the atmosphere. Because of that practical choice it is logical to also define the exergy of diffusion of liquid water by the exergy required for its release to the standard atmosphere.

Equation (37) can also be used to calculate the exergy of diffusion of liquid water. Even though there is no chemical change involved, the expression of the generic molecule can be used. Note that various attempts have been made in the literature [10], [4], [2] to find a global equilibrium between gaseous, liquid and solid species on Earth even going as far as considering various depth in the Earth crust¹.

Song et al. [9] developed new correlations based on a broad range of data bases. As a result of these various analyses the exergy of diffusion of liquid water varies between 5 et 950 kJ/kmol. Using the higher values results in a variation of the exergy values of fuels like hydrocarbons. From a practical standpoint this introduces complications that are not worth the efforts and we propose to limit the exergy of diffusion (chemical exergy in the literature) to the lower bound following the calculation shown below.

Example: Calculation of the exergy of diffusion of liquid water

We consider a system in which the water is evaporated and expanded in an isothermal turbine. For liquid water, a=0, b=2, c=1 and d=0. Equ. (37) becomes:

$$\bar{e}_{d, H_2O liq} = \left[\tilde{g}_{f H_2O liq}^0 - \frac{b}{2} \tilde{g}_{f H_2O g}^0 \right] + \tilde{r} T^0 \ln \left[\frac{1}{\left(\bar{c}_{H_2O}^A \right)^1} \right] = 5.1 \text{ [kJ/kmol]}$$

Conclusions

The concepts of fuel lower and higher heating values are compared with the fuel exergy value that has the advantage of being independent from the amount of condensation taking place in combustion or oxidation gases. The mechanistic model of reversible combustion presented allows a better interpretation of phenomena than a blind application of the concept of fuel exergy. Furthermore, and by coherence with First Law approaches it is recommended to separate the notions of exergy values for fuels from the concept of exergy of diffusion for chemically stable substances. In these definitions, one uncertainty remains that is linked to the broad range of exergy of diffusion of liquid water found in the literature.

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¹ Ertesvag [8] did a sensitivity analysis of the so-called chemical exergy for atmospheric gases with regards to variations of the ambient conditions. Regarding liquid and solids, Valero et al [7], updated the chemical exergies while proposing a new thermoecological-cost method

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