



METHODOLOGY FOR CALCULATING EXERGY IN CHEMICAL PROCESS

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ABSTRACT

This paper presents a methodology for calculating exergy in chemical processes. Its advantages, both in generality and ease of application, versus other procedures used until now are pointed out. To define the calculation methodology presented here we start from the fact that the chosen reference environment (RE) must satisfy the condition of internal equilibrium. It implies that the dead state of all the systems with the same atomic composition is identical. The RE model proposed by Gaggioli et al. (15, 16) is used. The temperature and pressure of the real physical environment are included as variables in the definition of the RE. Equations are derived to determine the chemical potential for the elements at the dead state as a function of these variables. As an example of the ease of applying the proposed method, procedures are given for calculating the exergy of the different types of substances found in a thermal power plant.

NOMENCLATURE

a	Specific non-flow exergy.
b	Specific exergy.
C_p	Specific heat at constant pressure.
e	Specific energy
LHV	Lower heating value.
HHV	Higher heating value.
h	Specific enthalpy.
P	Absolute pressure.
s	Specific entropy.
T	Thermodynamic temperature.
u	Specific internal energy.
v	Specific volume.
w_t	Technical (shaft) work.
μ	Chemical potential.
d	Atomic composition (vector).

x	Chemical composition (vector).
v	Generic reaction coefficients (vector).
Y	Air composition (vector).

Subscripts

0	Environmental state.
00	Dead state.
$i = 1, \dots, n$	Chemical species.
$I = 1, \dots, N$	
$j = 1, \dots, I$	Chemical element.
$k = 1, \dots, m = I$	Reference species.

Superscripts

0	Standard environmental state.
00	Standard dead state.

1. INTRODUCTION

Exergy analysis permits the true thermodynamic efficiency of industrial plants and processes to be determined, the primary causes of their inefficiency to be established, and the costs of obtaining their internal flows and products to be assigned in a rational way (1, 2).

Independently of the objective pursued in the exergy analysis, the first stage is to calculate the exergy of each and every one of the flows of mass and/or energy which define the logical thermodynamic structure of the production process at the aggregation level considered for analysis. In general, no more information is required than for the mass and energy balances of the subsystems (3, 4).

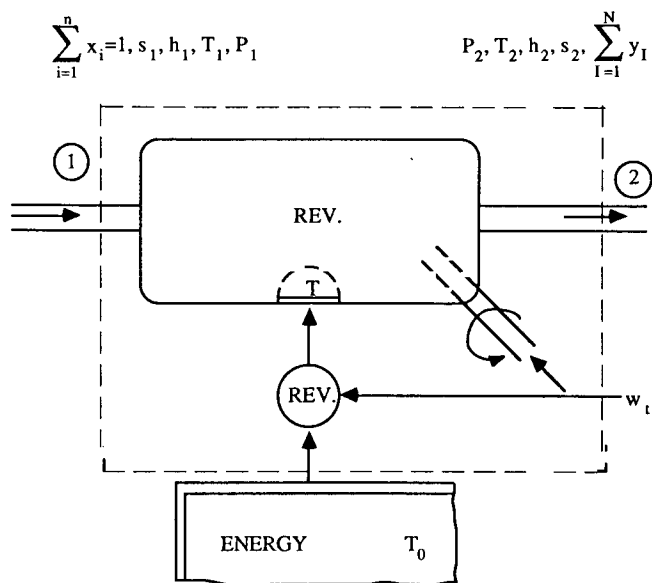


Fig. 2. Fully reversible steady-flow process involving a chemical reaction.

Consider the reversible process shown in Fig. 2, in which all the heat interactions are with the RE. The technical work required to produce the change of state $1 \rightarrow 2$ will be given by:

$$w_t = h_2 - h_1 - T_0 (s_2 - s_1) \quad (4)$$

For the exergy as defined to behave as a state function, the following must necessarily hold:

$$b_2 - b_1 = w_t \quad (5)$$

Using equations (1) and (4) the above equation leads to the following condition:

$$h_{2,00} - T_0 s_{2,00} = h_{1,00} - T_0 s_{1,00} \quad (6)$$

which is equivalent to that found by Ahrendts (8) and Siemons (9):

$$\sum_{i=1}^n x_i \mu_{i,00} = \sum_{i=1}^N y_i \mu_{i,00} \quad (7)$$

and which means that the RE must satisfy the condition of internal equilibrium.

Let us now see how to calculate the exergy, for which we will use Fig. 1, concentrating on how to define the chemical composition of the mass reservoir. Given the condition of internal equilibrium, in it there can physically exist a large number of chemical species. Furthermore, all the rest can be formed from the RE and in equilibrium with it (dead state) without the need to invest technical work. Let the set of components of the RE be the species k in Fig. 1. For a generic system with atomic composition d , we have shown that inde-

pendently of its thermodynamic state (P, T, x_i) , the chemical potential in its dead state $(\mu_{00} = h_{00} - T_0 s_{00} = u_{00} + P_0 v_{00} - T_0 s_{00})$ will be identical. Therefore, it can be calculated from any of the following equations:

$$\mu_{00} = \sum_{i=1}^n x_i \mu_{i,00} = \sum_{j=1}^l d_j \mu_{j,00} = \sum_{k=1}^m v_k \mu_{k,00} \quad (8)$$

Furthermore, the stoichiometric equation:

$$\sum_{i=1}^n r_{j,i} x_i = \sum_{k=1}^m r_{j,k} v_k = d_j \quad [j = 1, 2, \dots, l] \quad (9)$$

allows us to relate the vectors x , v and d , thus making Equation (8) operative. Furthermore, it indicates that the number of components must be equal to the number of chemical elements ($m=l$), and that every chemical element must be present in at least one of the components.

III. METHODOLOGY PROPOSED

The methodology proposed here for calculating the exergy is based on the suitably exploiting Equations (8) and (9).

Selecting the set of components.

Different approaches have been developed for formulating the chemical composition of the RE. Szargut (10) heads the list of authors who propose an RE which, while general and thus independent of the process analyzed, should be as similar as possible to the real physical environment. As this is not found in a state of perfect thermodynamic equilibrium, Szargut proposes the necessity of associating a single reference substance to each chemical element. The selection of the set of components (reference substances) becomes progressively more complicated as the number of chemical elements increases. The criteria of abundance and chemical stability in the real physical environment are the most commonly used in this selection (10-14). Szargut et al. (11, 12) have proposed reference substances for 50 elements, while Kameyama et al. (13) have done so for 79. The criteria used in selecting the reference substances are discussed in detail in their articles.

In processes which involve only the use or transformation of fossil fuels and their derivatives, there are only five major chemical elements: C, H, O, N and S. The RE model proposed by Gaggioli and Petit (15) and by Rodriguez (16) was used in the present work. In contrast with these authors, the pressure and temperature of the real physical environment are included as variables in the definition of the RE (see Table 1). The importance of this modification will be analyzed later in this paper.

Chemical potential of the reference substances $(\mu_{k,00})$.

For the condensed phases, the following is approximately true:

$$\mu_{k,00} = \Delta h_{f,k}^0 - T_0 s_k^0 + C_{P,k}^0 \left[T_0 - T^0 - T_0 \ln \left(\frac{T_0}{T^0} \right) \right] \quad (10a)$$

SUBSTANCE		STATE	Δh_f^0 (h ⁰) (cal/mol)	s^0 (cal/mol·K)	C_p^0 (cal/mol·K)	e_I^0 (lhv) (cal/mol)	e_{II}^0 (hhv) (cal/mol)	e_{III}^0 (cal/mol)	b^0 (cal/mol)
1 Carbon (graphite)	C	s	0	1.372	2.040	94052	94052	94052	98137
2 Hydrogen	H ₂	g	0	31.195	6.891	57796	68316	68316	56231
3	H	g	52098	27.391	4.968	80996	86256	86256	76697
4 Oxygen	O ₂	g	0	49.005	7.015	0	0	0	943
5	O	g	59559	38.470	5.237	59559	59559	59559	55866
6 Nitrogen	N ₂	g	0	45.769	6.961	0	0	0	159
7	N	g	112981	36.613	4.968	112981	112981	112981	108967
8 Sulfur (rhombic)	S	s	0	7.630	5.420	70960	70960	152032	143691
9 Calcium	Ca	s	0	9.970	6.300	-----	-----	194398	170216
10 Carbon Dioxide	CO ₂	g	-94052	51.070	8.870	0	0	0	4822
11 Water	H ₂ O	l	-68315	16.750	17.997	-10520	0	0	0
12	H ₂ O	g	-57796	45.106	8.025	0	10520	10520	2066
13 Sulfur Dioxide	SO ₂	g	-70960	59.290	9.530	0	0	81072	72884
14 Carbon Monoxide	CO	g	-26416	47.214	6.958	67636	67636	67636	65831
15 Calcite	CaCO ₃	s	-288450	22.200	19.570	-----	-----	0	0
16 Gypsum	CaSO ₄ ·2H ₂ O	s	-483060	46.360	44.500	-----	-----	0	0
17 Hydroxyl	OH	g	9310	43.890	7.143	38208	43468	43468	36768
18 Nitric Oxide	NO	g	21570	50.330	7.140	21570	21570	21570	21244
19 Carbonyl Sulfide	COS	g	-33900	55.320	9.920	131112	131112	212184	201896
20 Hydrogen Sulfide	H ₂ S	g	-5000	49.160	8.180	123756	134276	215348	191842
21 Ammonia	NH ₃	g	-11040	46.040	8.500	75654	91434	91434	80435
22 Methanol	CH ₃ OH	g	-48270	57.290	10.490	161374	182414	182414	172038
23 Methane	CH ₄	g	-17880	44.530	8.510	191764	212804	212804	198455
24 Ethane	C ₂ H ₆	g	-20250	54.850	12.590	341242	372802	372802	357087
25 Ethene	C ₂ H ₄	g	12540	52.410	10.260	316236	337276	337276	325073
26 Ethyne	C ₂ H ₂	g	54020	48.000	10.530	299920	310440	310440	302335
27 Propane	C ₃ H ₈	g	-24820	64.510	17.570	488520	530600	530600	513717
28 Propene	C ₃ H ₆	g	4880	63.800	15.270	460424	491984	491984	478096
29 n-Butane	C ₄ H ₁₀	g	-30150	74.120	23.290	635038	687638	687638	669601
30 n-Pentane	C ₅ H ₁₂	g	-35000	83.400	28.730	782036	845156	845156	826064

Reference [23]

Table 2. Energy and exergy of chemical elements and substances (REst)

- Pressure: Atmospheric pressure P_0
- Temperature: Atmospheric temperature T_0
- Reference substances:

Air (Relative humidity = 100%):

$$(j=4) \text{ N} \leftrightarrow (k=4) \text{ N}_2 \quad (\text{g}) \quad Y_{\text{N}_{2,00}} = 0.7898 (1 - Y_{\text{H}_2\text{O},00})$$

$$(j=3) \text{ O} \leftrightarrow (k=3) \text{ O}_2 \quad (\text{g}) \quad Y_{\text{O}_{2,00}} = 0.2099 (1 - Y_{\text{H}_2\text{O},00})$$

$$(j=1) \text{ C} \leftrightarrow (k=1) \text{ CO}_2 \quad (\text{g}) \quad Y_{\text{CO}_{2,00}} = 0.0003 (1 - Y_{\text{H}_2\text{O},00})$$

$$\text{H}_2\text{O} \quad (\text{g}) \quad Y_{\text{H}_2\text{O},00} = P_{\text{v,H}_2\text{O}}(T_0)/P_0$$

Condensed phases:

$$(j=2) \text{ H} \leftrightarrow (k=2) \text{ H}_2\text{O} \quad (\text{l})$$

$$(j=5) \text{ S} \leftrightarrow (k=5) \text{ CaSO}_4 \cdot 2\text{H}_2\text{O} \quad (\text{s})$$

$$(j=6) \text{ Ca} \leftrightarrow (k=6) \text{ CaCO}_3 \quad (\text{s})$$

$$\text{Ash} \quad (\text{s})$$

Table 1. Characteristics of the reference environment (exergy)

For the species present as gases in the RE, and assuming ideal gas behavior, we have:

$$\mu_{k,00} = \Delta h_{f,k}^0 - T_0 s_k^0 + C_{P,k}^0 \left[T_0 - T_0 \ln \left(\frac{T_0}{T} \right) \right] + R T_0 \ln \left(\frac{Y_{k,00} \cdot P_0}{P^0} \right)$$

Chemical potential of the elements ($\mu_{j,00}$).

Let there be a generic system with atomic composition: $C_c H_h O_o N_n S_s Ca_a$. Logically this corresponds to a multitude of systems with different chemical composition, all of which are characterized by the vector $dT = (c, h, o, n, s, a)$. The vector v , which expresses the stoichiometric relation (Eq. 9) between this system and the reference substances selected for the RE, is determined by solving the system of equations $r \cdot v = d$.

$$\begin{aligned} (k=1) \text{ CO}_2 &: v_1 = c + s - a \\ (k=2) \text{ H}_2\text{O} &: v_2 = h/2 - 2s \\ (k=3) \text{ O}_2 &: v_3 = -c + o/2 - h/4 - 3s/2 - a/2 \\ (k=4) \text{ N}_2 &: v_4 = n/2 \\ (k=5) \text{ CaSO}_4 \cdot 2\text{H}_2\text{O} &: v_5 = s \\ (k=6) \text{ CaCO}_3 &: v_6 = a - s \end{aligned} \quad (11)$$

The chemical potential of any system in its dead state can be calculated as a function of its v_k coefficients (Eq. 11) and from the chemical potential of the reference substances (Eq. 10) using the following equation:

$$\mu_{00} = \sum v_k \cdot \mu_{k,00} \quad (12)$$

By applying this to each of the chemical elements present in the RE, we get the expression of their chemical potential as a function of the variables P_0 and T_0 , which are shown in Table 3. The thermodynamic data used are from Table 2.

Calculating the exergy.

The conventional methods for calculating the exergy of a flow use expressions like:

$$b = h - T_0 s - \sum x_i \mu_{i,00} \quad (13a)$$

$$b = h - h_0 - T_0 (s - s_0) + \sum x_i (\mu_{i,0} - \mu_{i,00}) \quad (13b)$$

or other alternatives derived from these (15–20), which require the calculation of the terms $\mu_{i,00}$ and $(\mu_{i,0} - \mu_{i,00})$ for each and every one of the chemical species present in the process being analyzed. This is unnecessarily tedious and complicated, especially with variable reference environments.

The equation proposed here for evaluating the exergy:

$$b = h - T_0 s - \sum d_j \mu_{j,00} \quad (14)$$

allows the calculations corresponding to the RE selected ($\mu_{j,00}$) to be separated from those associated with the thermodynamic state of the mass flows (d_j , h and s). In this way it is sufficient to compute the values of $\mu_{j,00}$ once at the beginning of the calculation process in order to definitively solve the problem of determining the dead state of all the mass flows present in the installation. Another advantage of the proposed procedure is that it permits one to work easily and simply with different reference environments or with variable reference environments. This is due to the fact that the algorithms for calculating the thermodynamic properties, particularly the exergy of the mass flows, can be run independently of the RE selected.

IV. ENERGY

In calculating the energy of the mass flows, it is interesting to work with a reference environment which represents the physical environment, especially if the processes analyzed occur at temperatures above the atmospheric ones. Table 4 presents three possible reference environments for calculating the energy in this type of process. Note that the first is coherent with the definition of the lower heating value (LHV) of the fuels; the second is coherent with the higher heating value (HHV); and the last coincides with that used for calculating the exergy.

The energy of a mass flow is given by:

$$e(r) = h - h_{00}(r) \quad (15)$$

Using an analysis parallel to that done above for the exergy, it can be shown that if $e(r)$ must be a state function, then, once the RE has been defined, the value of $h_{00}(r)$ for all systems of equal atomic composition must be identical. That is:

$$h_{j,00}(\text{I}) = \Delta h_j(\text{I}) + \Delta C_{p,j}(\text{I}) \cdot (T_0 - T_0^0) \quad (\text{cal/mol})$$

$$h_{j,00}(\text{II}) = \Delta h_j(\text{II}) + \Delta C_{p,j}(\text{II}) \cdot (T_0 - T_0^0) \quad (\text{cal/mol})$$

$$h_{j,00}(\text{III}) = \Delta h_j(\text{III}) + \Delta C_{p,j}(\text{III}) \cdot (T_0 - T_0^0) \quad (\text{cal/mol})$$

$$\mu_{j,00} = \Delta h_j(\text{III}) - T_0 \Delta s_j + \Delta C_{p,j}(\text{III}) \cdot (T_0 - T_0^0 - T_0 \ln \frac{T_0}{T_0^0}) + R T_0 \ln \left[\left(Y_{\text{CO}_2,00} \cdot P_0 \right)^{e1} \left(Y_{\text{O}_2,00} \cdot P_0 \right)^{e3} \left(Y_{\text{N}_2,00} \cdot P_0 \right)^{e4} \right] \quad (\text{cal/mol})$$

	ENERGY (r = I)			ENERGY (r=II)			ENERGY (r = III) AND EXERGY					
	Δh_j	ΔC_{pj}	Δh_j	$\Delta C_{p,j}$	Δh_j	ΔC_{pj}	Δs_j	e1	e3	e4		
(j=1) C	- 94052	1.855	- 94052	1.855	- 94052	1.855	2.065	1	- 1	0		
(j=2) H	- 28898	2.259	- 34158	7.245	- 34158	7.245	- 3.876	0	- 1/4	0		
(j=3) O	0	3.508	0	3.508	0	3.508	24.502	0	1/2	0		
(j=4) N	0	3.481	0	3.481	0	3.481	22.885	0	0	1/2		
(j=5) S	- 70960	2.515	- 70960	2.515	- 152032	- 12.717	- 31.778	1	- 3/2	0		
(j=6) Ca	-----	-----	-----	-----	- 194398	1.702	- 53.373	- 1	- 1/2	0		

$$Y_{\text{CO}_2,00} = 0.0003 (1 - Y_{\text{H}_2\text{O},00}) ; Y_{\text{O}_2,00} = 0.2099 (1 - Y_{\text{H}_2\text{O},00}) ; Y_{\text{N}_2,00} = 0.7898 (1 - Y_{\text{H}_2\text{O},00})$$

$$Y_{\text{H}_2\text{O},00} = P_{\text{v,H}_2\text{O}}(T_0) = 217.99 \exp \left[\left(\frac{0.01}{T_0} \right) (374.16 - t_0) \sum_{i=1}^8 F_i (0.65 - 0.01 t_0)^{i-1} \right]$$

$$t_0 = T_0 - 273.15 ; F_1 = -741.9242 ; F_2 = -29.7210 ; F_3 = -11.55286 ; F_4 = -0.8685635$$

$$F_5 = 0.1094098 ; F_6 = 0.439993 ; F_7 = 0.2520658 ; F_8 = 0.05218684$$

Reference [24]

Table 3. Enthalpy and chemical potential of elements in the dead state (RE: P_0, T_0)

$$h_{00}(r) = \sum_{i=1}^n x_{i,00}(r) = \sum_{j=1}^l d_j h_{j,00}(r) = \sum_{k=1}^m v_k h_{k,00}(r)$$

• Pressure:	Atmospheric pressure P_0		
• Temperature:	Atmospheric temperature T_0		
• Reference substances:			
	$r = I$	$r = II$	$r = III$
(j=1) C \leftrightarrow (k=1)	CO ₂ (g)	CO ₂ (g)	CO ₂ (g)
(j=2) H \leftrightarrow (k=2)	H ₂ O (g)	H ₂ O (l)	H ₂ O (l)
(j=3) O \leftrightarrow (k=3)	O ₂ (g)	O ₂ (g)	O ₂ (g)
(j=4) N \leftrightarrow (k=4)	N ₂ (g)	N ₂ (g)	N ₂ (g)
(j=5) S \leftrightarrow (k=5)	SO ₂ (g)	SO ₂ (g)	CaSO ₄ · 2H ₂ O (s)
(j=6) Ca \leftrightarrow (k=6)	-----	-----	CaCO ₃ (s)
	-----	Ash (s)	-----

Table 4. Characteristics of the reference environment (energy)

For this reason, the procedure for calculating the energy must be parallel to that used for calculating the exergy, and the expression for calculating $h_{k,00}(r)$ is given by:

$$h_{k,00}(r) = \Delta h_{f,k}^0(r) + C_{P,k}^0(r) \cdot (T_0 - T^0) \quad (17)$$

The coefficients v_k of the generic system $dT = (c, h, o, n, s, a)$ will be those expressed in Equation 11 when $r = III$. Solving the system of equations $r \cdot v = d$ corresponding to the other reference environments, we get their associated coefficients:

$$\begin{aligned} (k=1) \text{ CO}_2 &: v_1 = c \\ (k=2) \text{ H}_2\text{O} &: v_2 = h/2 \\ (k=3) \text{ O}_2 &: v_3 = -c + o/2 - h/4 - s \\ (k=4) \text{ N}_2 &: v_4 = n/2 \\ (k=5) \text{ SO}_2 &: v_5 = s \\ (k=6) \text{ -----} &: \text{-----} \end{aligned} \quad (18)$$

Table 3 gives the expressions for calculating the $h_{j,00}(r)$ corresponding to the elements as a function of the variables defining the RE. Logically, the equation to use for calculating the energy, according to the methodology proposed here, will be:

$$e(r) = h - \sum d_j \cdot h_{j,00}(r) \quad (19)$$

V. THE EFFECT OF ENVIRONMENT CONDITIONS

The question arising now is the following:

If to calculate the exergy, the fixed values of $P^0 = 1$ atm. and $T^0 = 298.15$ K which correspond to the standard reference environment (REst) are used, how big is the error involved?

In the case of destroyed exergy, the relative error will be $(T^0 - T_0)/T_0$, while for a heat flow at temperature T , it will be given by $(T_0 - T^0)/(T - T_0)$. Tables 5 and 6 give their numerical values for different environment conditions.

	$t_0 = 5^\circ\text{C}$	$t_0 = 15^\circ\text{C}$	$t_0 = 25^\circ\text{C}$	$t_0 = 35^\circ\text{C}$
Exergy Destruction	7.20 %	3.47 %	—	- 3.25 %

Table 5. Relative error for the calculated exergy destruction when REst is assumed.

	$t_0 = 5^\circ\text{C}$	$t_0 = 15^\circ\text{C}$	$t_0 = 25^\circ\text{C}$	$t_0 = 35^\circ\text{C}$
T = 100 K	11.23 %	5.31 %	—	- 4.80 %
T = 200 K	25.59 %	11.34 %	—	- 9.25 %
T = 600 K	- 6.21 %	- 3.21 %	—	3.43 %
T = 1200 K	- 2.17 %	- 1.10 %	—	1.12 %

Table 6. Relative error for the calculated exergy of heat flows when REst is assumed.

For fuels, the contribution of the physical component to the exergy is negligible except for very high pressures and temperatures, which are not very frequent in practice. Thus, we will analyze only their chemical component. This is given by:

$$b_0 = h_0 - T_0 s_0 - \sum d_j \mu_{j,00} \quad (20)$$

In the case where the reference environment is the standard one, the exergy:

$$b^0 = h^0 - T^0 s^0 - \sum d_j \mu_j^{00} = \Delta h_f^0 - T^0 s^0 - \sum d_j \mu_j^{00}$$

is named standard chemical exergy. Drawing parallels with the standard chemical energy:

$$e^0(r) = h^0 - \sum d_j h_j^{00}(r) = \Delta h_f^0 - \sum d_j h_j^{00}(r) \quad (22)$$

When the RE's used to calculate energy and exergy coincide, that is when $r=III$ in our case, Kotas (18) gives the name enthalpy of devaluation to $e^0(r)$, and therefore $e^0(III)$ is the standard enthalpy of devaluation. Furthermore, it is clear that $e^0(I)=LHV$ and $e^0(II)=HHV$.

Table 7 gives the values of μ_j^{00} and $h_j^{00}(r)$ obtained for the REst using the equations proposed in Table 3.

		Lignite	Subbitum.	Bituminous	Anthracite	Fuel-Oil 1	Fuel-Oil 2	Fuel-Oil 4	Fuel-Oil 6
Ultimate Analysis:	• Carbon	0.389	0.588	0.687	0.809	0.865	0.864	0.861	0.857
	• Hydrogen	0.027	0.038	0.045	0.030	0.132	0.127	0.119	0.105
	• Oxygen	0.089	0.122	0.076	0.024	0.002	0.002	0.004	0.008
	• Nitrogen	0.006	0.013	0.016	0.010	0.000	0.000	0.001	0.002
	• Sulfur	0.053	0.003	0.012	0.005	0.001	0.007	0.015	0.028
	• Moisture	0.238	0.196	0.080	0.021				
	• Ash	0.198	0.040	0.084	0.101				
HHV (kcal/kg)		3915	5630	6740	7490	11080	10870	10500	10140
Atomic Composition	• Carbon	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
	• Hydrogen	0.8271	0.7701	0.7805	0.4419	1.8183	1.7515	1.6469	1.4600
	• Oxygen	0.1718	0.1558	0.0830	0.0223	0.0017	0.0017	0.0035	0.0070
	• Nitrogen	0.0132	0.0189	0.0199	0.0105	0.0000	0.0000	0.0010	0.0020
	• Sulfur	0.0510	0.0019	0.0066	0.0023	0.0004	0.0030	0.0065	0.0122
	• Moisture	0.4079	0.2222	0.0776	0.0173				
	• Ash (g/mol C)	6.1136	0.8171	1.4686	1.4995				
f Δh_f^0 s^0	(mol C/kg)	32.387	48.955	57.198	67.355	72.017	71.934	71.684	71.351
	(cal/mol C)	- 5040	- 5490	- 3340	1890	- 2340	- 2980	- 4290	- 2680
	(cal/mol C:K)	5.660 (25)	4.969 (25)	4.713 (25)	3.271 (25)	9.147 (26)	8.907 (26)	8.559 (26)	7.912 (26)
e_I^0	(cal/mol C)	112240	108620	112920	108700	144290	141900	137810	134440
	(kcal/kg)	3635	5315	6460	7320	10390	10210	9880	9590
e_{II}^0	(cal/mol C)	120880	115000	117840	111200	153850	151110	146480	142110
	(kcal/kg)	3915	5630	6740	7490	11080	10870	10500	9590
e_{III}^0	(cal/mol C)	125020	115160	118370	111390	153890	151360	147010	143210
	(kcal/kg)	4050	5640	6770	7505	11080	10890	10540	10210
b^0	(cal/mol C)	127800	118430	121120	114530	153140	150760	146650	143210
	(kcal/kg)	4140	5800	6930	7715	11030	10840	10510	10220

Table 8b. Energy and exergy of hydrocarbon fuels (REst)

	h_j^{∞} (I) (cal/mol)	h_j^{∞} (II) (cal/mol)	h_j^{∞} (III) (cal/mol)	μ_j^{∞} (cal/mol)
(j=1) C	-94052	-94052	-94052	-98548
(j=2) H	-28898	-34158	-34158	-32766
(j=3) O	0	0	0	-7777
(j=4) N	0	0	0	-6902
(j=5) S	-70960	-70960	-152032	-145966
(j=6) Ca	----	----	-194398	-173189

Table 7. Enthalpy and chemical potential of the elements in the dead state (REst)

Table 2 gives the standard chemical energy and exergy for the different substances, while Table 8 contains these variables for different fossil fuels.

• Natural gas analysis		• Atomic composition	
	x_i		d_j f_j
i = 1 CH ₄	0.9225	j = 1	1.0730 1.0000
i = 2 C ₂ H ₆	0.0653	j = 2	4.1340 3.8527
i = 3 C ₃ H ₈	0.0055	j = 3	0.0002 0.0002
i = 4 C ₄ H ₁₀	0.0007	j = 4	0.0116 0.0108
i = 5 C ₅ H ₁₂	0.0001	• Conversion factor	
i = 6 N ₂	0.0058	f = 47.872 mol C / Nm ³	
i = 7 CO ₂	0.0001		
• Energy and Exergy			
HHV = 10050 · 10 ³ cal/Nm ³		hhv = 209935 cal/mol C	
		Δh _f ⁰ = -15715 "	
9080 · 10 ³	"	c _I ⁰	189670 "
10050 · 10 ³	"	c _{II} ⁰	209935 "
10050 · 10 ³	"	c _{III} ⁰	209935 "
9400 · 10 ³	"	b ⁰	196375 "

Table 8a. Energy and exergy of natural gas (REst).

The variation in the chemical exergy of fuels, $(b^0 - b_0)/b_0$, with the physical environment's pressure and temperature is shown in Table 9.

Finally, Table 10 gives the values of the exergy for a flow of combustion gas, one of air, and two of water, together with the errors introduced by calculating their exergy with respect to the REst.

P_0 (atm)	t_0 (°C)	Natural Gas	Fuel-Oil No. 1	Lignite
1	5	- 0.48 %	- 0.04 %	0.14 %
1	15	- 0.24 %	- 0.02 %	0.07 %
1	25	196373 cal/mol	153137 cal/mol	127796 cal/mol
1	35	0.24 %	0.02 %	- 0.07 %
0.9	25	0.06 %	0.02 %	0.01 %
0.8	25	0.13 %	0.04 %	0.02 %

Table 9. Relative error for the calculated exergy of fuels when REst is assumed.

		Gas	Air	Water	Steam
Pressure	(atm)	0.95	0.95	121.9	121.9
Temperature	(K)	600	600	600	600
Composition:	N ₂ (%)	70.00	77.90	Saturated liquid	Saturated vapor
	O ₂ (%)	5.00	20.70		
	CO ₂ (%)	10.00	---		
	H ₂ O (%)	12.00	1.40		
	CO (%)	1.00	---		
	SO ₂ (%)	1.00	---		
P_0 (atm)	t_0 (°C)	b (cal/mol)	b(cal/mol)	b (kcal/kg)	b (kcal/kg)
1	5	- 6.7 %	- 13.8 %	- 12.5 %	- 9.1 %
1	15	- 3.4 %	- 7.0 %	- 6.5 %	- 4.7 %
1	25	2373.4	642.0	110.2	251.6
1	35	3.2 %	6.5 %	7.2 %	5.0 %
0.9	25	- 2.3 %	- 9.0 %	0.0 %	0.0 %
0.8	25	- 4.7 %	- 17.4 %	0.0 %	0.0 %

Table 10. Relative error for the calculated exergy of mass flows when REst is assumed.

As can be seen in Tables 5, 6, 9 and 10, except for the case of fuels, the error introduced by calculating the exergy using the standard reference environment is considerable, especially when the real environment temperature differs from T^0 .

Let us take the case of a thermal generating station. Its exergy efficiency is given by the ratio between the electric power produced and the exergy of the fuel used in the process. Since the former does not at all depend on environment conditions, and the latter's variation with T_0 and P_0 is not significant, then the error introduced by working with REst is practically zero. Nevertheless, although the size of the total irreversibility (destroyed exergy+lost exergy) is hardly modified, its distribution can be greatly altered. For example, if $P_0 < P^0$ and $T_0 < T^0$, the exergy losses in the flue gases and in heat given up by the condenser will be underestimated, while the exergy destroyed by internal irreversibilities will be overestimated. Therefore, the exergy efficiency of the individual subsystems which make up the thermal generating

station, the exergies of the flows (and their exergetic costs) and any concepts of efficiency loss which may be defined will not display their true numerical values if the RE does not strictly satisfy the real environment conditions.

VI. CONCLUSIONS

This paper has presented a precise methodology for calculating the exergy of substances which are of industrial importance. Although all the bases had been laid previously, in our opinion clear systematics needed to be developed in order to eliminate the difficulties arising from transferring to the calculation procedure concepts such as that of component, which, though useful in making the physical meaning of the exergy clear, increases the complexity and adds ambiguities to the calculation procedure. The advantages of the proposed methodology come from exploiting the fact that the exergy is a state function, once the RE has been defined, with the result that it does not need to be calculated throughout a preset trajectory or process, as occurs when determining the total exergy from its components (physical, mechanical, thermal, chemical,...). Furthermore, it must be remembered that although in calculating the exergy, a given combination of reversible processes between the system's dead state and its real state can be followed, and mathematically one can therefore speak of components, this does not imply that the separation of the total exergy into the partial contributions of these components will always have a strict physical meaning.

As stated by Wepfer and Gaggioli (14), the choice of RE must be made after a careful study of the plant to be analyzed and of the environment with which it interacts. There is no unique reference environment which is at the same time universal and also the most suitable for all processes. This conclusion should direct our efforts to facilitating the calculation of exergy. The methodology presented here separates the calculations corresponding to the RE ($\mu_{j,00}$) from those associated with the thermodynamic state of the mass flows (h and s), which is a clear advantage if one accepts the possibility of changing the RE or of introducing variables into its definition. From this conclusion we also learn that, in the case of fossil fuels, it is more useful to develop equations for Δh_i^0 and s_i^0 which can be used for any RE, rather than directly drawing the correlations which give us b^0 with respect to a specific reference environment.

We agree with Rosen and Scott (21) in that in designing a plant, it is sufficient to use an RE defined by the average values of P_0 and T_0 in the site where it is to be installed, or if the design is generic (its location has not been decided, or it is not yet going to be considered) it will be sufficient to use the REst. On the other hand, when the plant is already installed and we wish to know the state of its real functioning at any time by using performance tests (4, 22) to compare with the design conditions, it is essential that the RE be defined with respect to the specific environment in which the process occurs.

VII. REFERENCES

1. Gaggioli, R.A. Second Law Analysis for Process and Energy Engineering. *ACS Symposium Series*, No. 235, 1983, pp. 3-50.
2. Valero, A., Lozano, M.A., Muñoz, M. A General Theory of Exergy Saving (I. On the Exergetic Cost). *ASME, WAM 1986, AES-Vol. 2-3*, pp. 1-8.
3. Valero, A., Guallar, J., Muñoz, M. The Exergetic Cost and Related Concepts. An application to a Simple Cogeneration Plant. *Second Law Analysis of Thermal Systems*, ASME Book 100236, 1987, pp. 123-130.
4. Lozano, M.A., Valero, A. Application of the Exergetic Cost Theory to a Steam Boiler in a Thermal Generating Station. *ASME, WAM 1987, AES-Vol. 3-2*, pp. 41-51.
5. Kestin, J. Availability: The Concept and Associated Terminology. *Energy*, Vol. 5, 1980, pp. 679-692.
6. Haywood, R.W. *Equilibrium Thermodynamics*. Wiley, Chichester, 1980.
7. Kotas, T.J. Exergy Concepts for Thermal Plant. *Int. J. Heat and Fluid Flow*, Vol. 2, 1980, pp. 105-114.
8. Ahrendts, J. Reference States. *Energy*, Vol. 5, 1980, pp. 667-677.
9. Siemons, R.V. Interpretation of the Exergy Equation for Steady-Flow Processes. *Energy*, Vol. 11, 1986, pp. 237-244.
10. Szargut, J. International Progress in Second Law Analysis. *Energy*, Vol. 5, 1980, pp. 709-718.
11. Szargut, J., Dzięziniewicz, C. Energie utilisable des substances chimiques inorganiques. *Entropie*, No. 40, 1981, pp. 14-23.
12. Morris, D.R., Szargut, J. Standard Chemical Exergy of Some Elements of the Planet Earth. *Energy*, Vol. 11, 1986, pp. 733-755.
13. Kameyama, H. et al. Evaluation of Reference Exergies for the Elements. *Applied Energy*, Vol. 11, 1982, pp. 69-83.
14. Wepfer, W.J., Gaggioli, R.A. Reference Datums for Available Energy. *ACS Symposium Series*, No. 122, 1980, pp. 77-92.
15. Gaggioli, R.A., Petit, P.J. Second Law Analysis for Pinpointing the True Inefficiencies in Fuel Conversion Systems. *ACS Symposium Series*, No. 21, 1976, pp. 56-75.
16. Rodriguez, L. Calculation of Available-Energy Quantities. *ACS Symposium Series*, No. 122, 1980, pp. 56-75.
17. Moran, M.J. *Availability Analysis*. Prentice-Hall, Englewood Cliffs, 1982.
18. Kotas, T.J. *The Exergy Method of Thermal Plant Analysis*. Butterworths, London, 1985.
19. Lozano, M.A., Valero, A. Determinación de la exergía para sustancias de interés industrial. *Ingeniería Química*, Marzo 1986, pp 119-128.
20. Marín, J.M., Turégano, J.A. Contribution to the Calculation of Chemical Exergy in Industrial Processes (Electrolyte Solutions). *Energy*, Vol. 11, 1986, pp. 231-236.
21. Rosen, M.A., Scott, D.S. On the Sensivities of Energy and Exergy Analyses to Variations in Dead-State Properties. *ASME, WAM 1987, AES-Vol. 3-1*, pp. 23-32.
22. Valero, A., et al. GAUDEAMO: A System for Energetic/Exergetic Optimization of Coal Power Plants. *ASME, WAM 1986, AES-Vol. 2-1*, pp. 43-49.
23. Karapetyans, M. Kh. *Chemical Thermodynamics*. Mir, Moscú, 1978.
24. *Ashrae Handbook, 1977 Fundamentals*. Ashrae, New York, 1977.
25. Eisermann, W., Johnson, P., Conger, W.L. Estimating Thermodynamic Properties of Coal, Char, Tar and Ash. *Fuel Processing Technology*, Vol. 3, 1980, pp. 39-53.
26. Ikumi, S., Luo, C.D., Wen, C.Y. A Method of Estimating Entropies of Coal and Coal Liquids. *The Canadian Journal of Chemical Engineering*, Vol. 60, 1982, pp. 551-555.