

THE EXERGY ANALYSIS OF THE INDUSTRIAL SYSTEMS

Ilie SIMINICEANU^{1,2}

¹Corresponding Member of the Romanian Academy of Technical Sciences,

²“Gh. Asachi” Technical University of Iași

Abstract: This paper deals with the exergy analysis of a nitric acid plant with ammonia oxidation at normal pressure, and chemical absorption at a pressure of 5 bar (1/5 process). The exergy balance model established previously for open chemical systems, and the corresponding exergy efficiency have been used, together with the measured values of operating parameters (temperatures, pressures, flow rates, and concentrations). The exergy efficiency of the 1/5 nitric acid plant determined in this work is 30.52%. The total exergy lost and destructed by irreversibility was 5156 kW from the 7421 kW input. The largest contributions had the ammonia oxidation reactor (44.97%), the absorption – reaction column (20.17%), the steam over heater (19.05%), the water pre-heater (5.77%), and the turbine (4.50%). The ways to improve the efficiency of these operations are also discussed.

Keywords: exergy balance, exergetic efficiency, exergy destroyed, exergy lost, nitric acid plant.

1. INTRODUCTION

Traditionally, most of the industrial systems have been designed using the energetic performance criteria based on the first law of thermodynamics only. Exergy analysis combines the first and the second laws of thermodynamics, and is a powerful tool for analyzing both quantity and the quality of energy utilization. Today, the exergy is considered the best global energy sustainability indicator [1]. The word *exergy* was introduced by *Zoran Rant* (1904- 1972), and defined as the maximum “technical available work” obtainable while the system communicates with the environment reversibly [2]. The exergy analysis method has been extended to chemical and metallurgical processes due to the method and values of standard chemical exergy of substances published by Kotas [4] and Szargut[5]. Some authors avoided the word “exergy” by using “availability” or “second law analysis [3, 6]. Finally American school accepted the term “exergy” which was consecrated through the international journal with the same name. In Romania, the method was first applied to ammonia manufacture processes [7, 8]. In September 2014, *Science direct* indicated 14236 published works on “exergy analysis”, 1299 before 1995 with a maximum of 1852 papers in 2014. A steady increase of number of works reveals the importance of the subject. Recent works recognize the usefulness of the exergy function as a global energy sustainability indicator, as well as for the environmental impact estimation [1, 9].

Among the numerous works on exergy analysis, there are a few papers dedicated to the nitric acid manufacturing plants [10, 11, 12]. The first is due to Professor Denbigh, recognized as a “founding fathers” of *Chemical Reaction Engineering*. His pioneering paper [10] is cited by Riekert [11]. Denbigh discussed the importance of the “second law efficiency of the chemical processes”, and gave as example the nitric acid manufacture. He used a simplified “black box” of the plant and obtained a “second law efficiency” of 6.0 %. This means that 94% of exergy, a measure of energy quality, was destroyed. This could be unbelievable because any nitric acid production plant is self sufficient in energy. Moreover, it is a net exporter of energy. For each tone of nitric acid, the plant generates 0.5 to 1.4 tones of steam with 42 bar and 673 K. The second who applied „the availability” analysis to a nitric acid plant was Professor Riekert [11]. He used a more detailed analysis, taking into account the previous synthesis of ammonia from methane, air and water. For the nitric acid manufacture, using an absorption column at 5 bar, he obtained an exergy efficiency of 15.53 %. Finally, we must mention a more recent work [12] where the exergy efficiency of a isobaric high pressure 10/10 nitric acid plant was 24.71%.

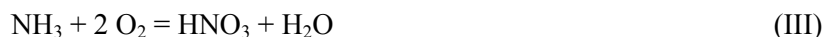
In this paper, the exergy analysis of a 1/5 nitric acid plant is carried out. The measured and calculated quantities are presented in the tables 1 to 3. The equations used for calculations are derived and presented in the Annex. The overall exergy efficiency of the nitric acid process was of 30.52 %.

2. EXPERIMENTAL AND COMPUTING METHODS

The measurements have been done on the full scale nitric acid plant presented in Fig.1. This implies two chemical transformations: ammonia oxidation on a platinum- rhodium (5 to 10 % rhodium) gauge as catalyst (I), and nitric oxide absorption- oxidation in water (II) :



The overall reaction (III= I + II) is:



The two transformations can be operated at pressures varying from 1 to 10 bars. The stoichiometry shows that equilibrium of (I) needs low pressure, while (II) is intensified by high pressure. Therefore, the old isobaric (1/1) plant was replaced by “dual” 1/5 plants. Pressure was steadily increased in both steps to intensify processes and reduce the volume of equipment. Therefore, plants 5/5 or 5/10 are also possible. In the last, absorption takes place at 10 bar, absorption is enhanced, and NO_x emissions are reduced.

The 31 material fluxes (noted with circles in Fig 1) are presented in the table 1, all in mol/s. The block diagram bellow the figure1 has only the inputs and outputs of the plant. The inputs are: ammonia gas (1), primary air for ammonia oxidation (2), secondary air for NO oxidation to NO₂ (3), process water for nitric oxide absorption (4). There is also the electricity (pure exergy) to drive the compressors C₁- C₃ and the condense pump. The outlets are: the nitric acid (5), the 42 bar steam (10), and the waste gas (6). The intermediate flow rates have been obtained from the material balance of each operation. The first two columns of the table 1 include the measured pressure and temperature of each material flux.

Table 1. Experimental operating parameters, and calculated exergies.

Flux	T, K	P, bar	Flow rate mol/s						Exergy kW
				N ₂	O ₂	NO	H ₂ O	HNO ₃	
1	298	1.01	19.20	-	-	-	-	-	6488
2	298	1.01	139.79	108.11	28.78	-	2.94	-	-
3	298	1.01	63.35	49.00	13.02	-	1.33	-	-
4	298	1.01	9.29	-	-	-	9.29	-	8
5	298	5.00	50.01	-	-	-	31.64	18,37	568
6	292	1.01	163.46	157.43	4.30	0.19	1.54	-	83
7	298	45.00	78.52	-	-	-	78.52	-	6
8	417	44.50	78.52	-	-	-	78.52	-	81
9	498	44.00	78.52	-	-	-	78.52	-	169
10	673	42.00	78.52	-	-	-	78.52	-	1703
11	311	1.15	19.20	-	-	-	-	-	6495
12	321	1.20	139.79	108.43	28.78	-	2.94	-	63
13	473	1.15	139.79	108.43	28.78	-	2.94	-	198
14	1206	1.12	163.91	108.43	5.06	18.56	31.86	-	4347
15	658	1.09	163.91	108.43	5.06	18.56	31.86	-	2322
16	513	1.06	163.91	108.43	5.06	18.56	31.86	-	1949
17	388	1.03	163.91	108.43	5.06	18.56	31.86	-	1730
18	305	1.01	163.91	108.43	5.06	18.56	31.86	-	1581
19	305	1.01	138.58	108.43	5.06	18.56	6.53	-	1558

Table 1 (continued)

Flux	T, K	P, bar	Flow rate mol/s	N ₂	O ₂	NO	H ₂ O	HNO ₃	Exergy kW
20	303	1.01	201.93	157.43	18.08	18.56	7.86	-	1527
21	514	5.20	201.93	157.43	18.08	18.56	7.86	-	2666
22	427	5.15	201.93	157.43	18.08	18.56	7.86	-	2471
23	339	5.10	201.93	157.43	18.08	18.56	7.86	-	2352
24	305	5.00	201.93	157.43	18.08	18.56	7.86	-	2308
25	305	5.00	195.92	157.43	18.08	18.56	1.85	-	2303
26	305	5.00	163.46	157.43	4.30	4.30	1.54	-	731
27	415	4.80	163.46	157.43	4.30	4.30	1.54	-	801
28	305	1.01	25.33	-	-	-	25.33	-	23
29	305	5.00	25.33	-	-	-	25.33	-	23
30	305	5.00	6.01	-	-	-	6.01	-	5
31	305	5.00	31.34	-	-	-	31.34	-	28

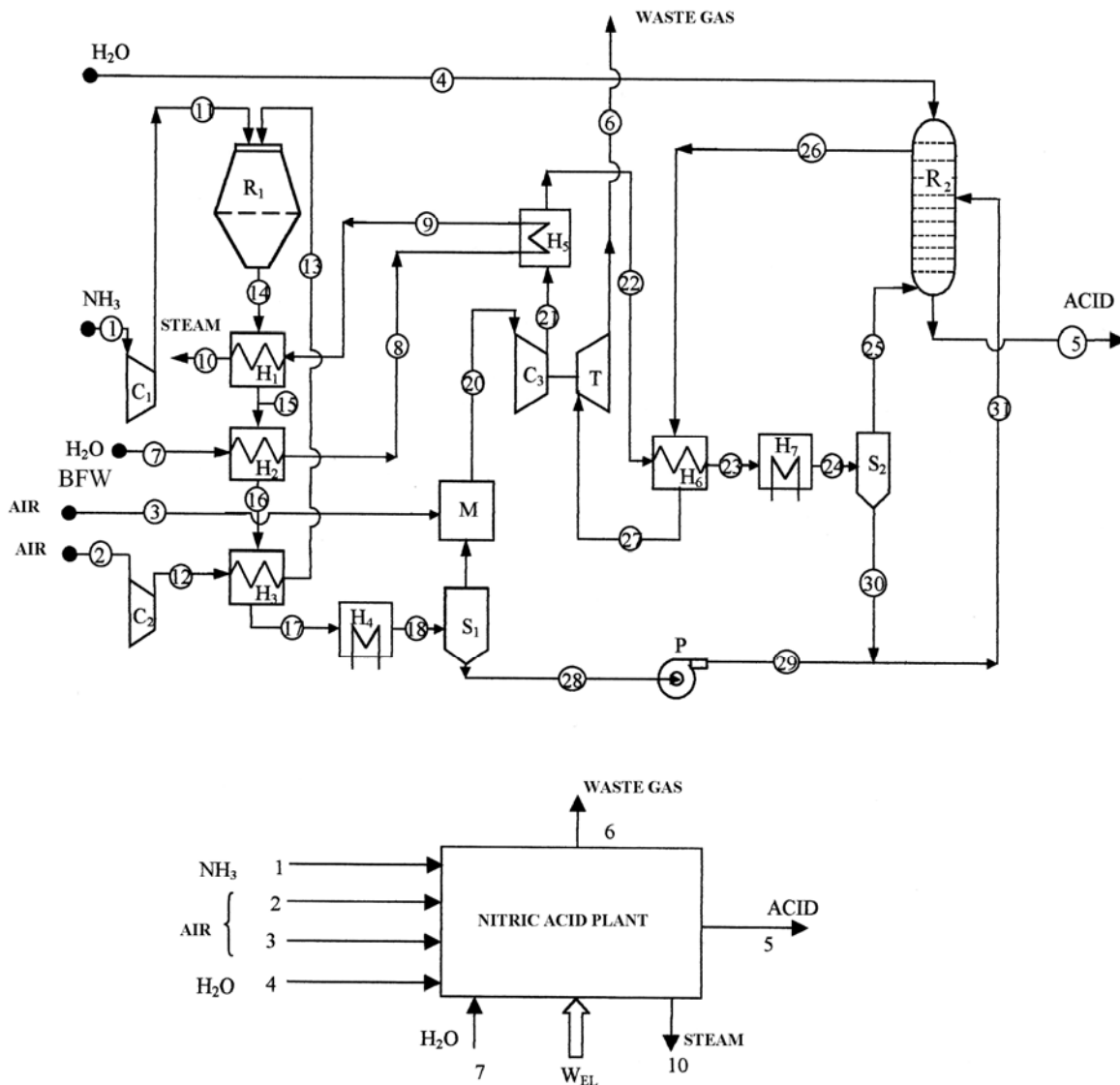


Fig. 1. Bloc diagram of the nitric acid plant:

C1- ammonia blower, C2 – primary air compressor, C3 – secondary air compressor, T – turbine, P – condense pump, R1 – ammonia oxidation reactor, R2 – absorption-reaction column, M – mixing device, S1-S2 – condense separators, H1-H7 – heat exchangers.

3. RESULTS

The last column of the table 1 contains the calculated exergy for each flux. The standard chemical exergies tabulated by Szargut et al.[5] have been used. In the case of ammonia, at environment temperature and pressure, the total exergy equals the chemical exergy: $19,20 \text{ mol/s} \times 337,90 \text{ kJ/mol} = 6488 \text{ kJ/s}$. For the secondary air (21) the total exergy is reduced to the physical component having the chemical composition identical to standard environment, but different temperature (514 K) and pressure (5.2 bar).

Table 2. Overall exergy balance of the nitric acid plant

Flux	$E, \text{ kW}$	%	Flux	$E, \text{ kW}$	%
1 Ammonia	6488	87.43	5. Acid	568	7.66
4. Process water	8	0.11	10. Steam	1703	22.87
Electricity			Lost exergy	5150	69.47
-Compressor C1	10	0.13	$\eta_E = 0.3052$		
-Compressor C2	103	1.39			
- Compressor C3	812	10.94			
Total	7421	100.00	Total	7421	100.00

Table 3 presents the exergy destroyed (E_D) and the exergy lost (E_L) in the unit operations of the analyzed nitric acid plant. The equations derived in the Annex have been applied. The highest inefficiencies have the following five operations:

- Ammonia oxidation reactor (“the burner”) 44.97% of the total irreversibility ;
- Absorption- oxidation reactor (“the column”) 20.17 %;
- The super- heater of the steam 10.05;
- The water pre- heater 5.77 %
- The turbine 4.50 %.

 Table 3. Exergy destroyed (E_D) and exergy lost (E_L) in the unit operations of the nitric acid plant

Nr.	Flux	$E_D, E_L \text{ kW}$	Ψ	%	Φ	%
1	Waste gas 6	83		1.12		1.61
2	Ammonia compressor C1					
	- Electro-mechanic lost	1		0.01		0.05
	- Internal destructions	2		0.03		
3	Air compressor C2					
	- Electro-mechanic lost	10		0.13		0.77
	- Internal destructions	30		0.40		
4	Gas compressor C3					
	- Electro-mechanic lost	41		0.55		3.08
	- Internal destructions	118		1.59		
5	Turbine					
	- Electro-mechanic lost	99		1.33		4.50
	- Internal destructions	133		1.79		
6	Super heater	518		6.98		10.05
7	Oxidation reactor R1					
	- Heat lost	132		1.78		44.97
	- internal irreversibility	2187		29.47		
8	Water pre- heater H2	298		4.02		5.77
9	Air pre- heater H3	84		1.13		1.63
10	Gas cooler H4	149		2.01		2.89
11	Mixer M	31		0.42		0.60
12	Water pre- heater H5	107		1.44		2.07
13	Heat recover H6	49		0.66		0.95
14	Gas cooler H7	44		0.59		0.85
15	Absorption- reaction column R2	1040		14.02		20.17
	TOTAL	5156		69.48		100.00

4. CONCLUSIONS

The exergy method is illustrated for a nitric acid plant as industrial system. The exergy efficiency obtained (30.52 %) is higher than that obtained previously by Riekert (15.53 %)[11]. The difference has at least two reasons: (a) Riekert considered the input ammonia in liquid state. Therefore his E_1 includes the vaporisation enthalpy of ammonia. In our plant, the initial ammonia is gaseous; (b) The Riekert plant is not described in his paper. Nevertheless it must be of an older generation because it generated 3.3 folds less steam (per tone of nitric acid) than ours. With these corrections, the Riekert's efficiency would be of over 33.0 %.

The main exergy destructor of the nitric acid plant is the ammonia oxidation process, with a contribution of 45 % to the total irreversibility. This is a catalytic burning at almost 1200 K. The next transformation step, the absorption column, requires temperatures as low as possible. Such a variation of temperature always decrease the exergy efficiency.

A similar situation is in the heating systems of residential buildings. Here, the boiler has a flame temperature of up to 1273 K although the room radiators require only 343 K. Therefore it has very low exergy efficiency. That is why, in Germany the boilers have been replaced, experimentally, by fuel cells [13]. In fact, the world energy system has an exergy efficiency of only few percent (< 5%). The entire strategy of energetics must be changed for sustainability.

APPENDIX

A1. Exergy Balance in Closed Systems

The equation of exergy balance is obtained by coupling the energy balance (1) with the entropy balance (2).

$$(U_2 - U_1) + (E_{K_2} - E_{K_1}) + (E_{P_2} - E_{P_1}) = \int_1^2 \delta Q - W \quad (1)$$

$$S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T} \right)_F + S_{gen} \quad (2)$$

Indices 1 and 2 are for initial and final states of the system, while F for the frontier of the system. The equation (2) is multiplied by the temperature of the standard environment T_0 , then is subtracted from (1). The equation (3) is obtained:

$$\begin{aligned} & (U_2 - U_1) + (E_{K_2} - E_{K_1}) + (E_{P_2} - E_{P_1}) - T_0 (S_2 - S_1) = \\ & = \int_1^2 \delta Q - T_0 \int_1^2 \left(\frac{\delta Q}{T} \right)_F - W - T_0 S_{gen} \end{aligned} \quad (3)$$

The exergy variation ($E_2 - E_1$) is the sum::

$$E_2 - E_1 = (U_2 - U_1) + (E_{K_2} - E_{K_1}) + (E_{P_2} - E_{P_1}) - T_0 (S_2 - S_1) + P_0 (V_2 - V_1) \quad (4)$$

By introducing (3) in (4), results:

$$\{E_2 - E_1\} = \left\{ \int_1^2 \left(1 - \frac{T_0}{T} \right) \delta Q - [W - P_0 (V_2 - V_1)] \right\} - \{T_0 S_{gen}\} \quad (5)$$

Equation (5) is the exergy balance in a closed system. Each term is measured in J. In a discontinuous chemical process, the left side of (5) is the exergy change due to the reaction mixture

introduced in the reactor for a batch. The exergy change of this mixture depends only on the states 1 and 2. For ideal mixtures, the additive rule may be applied:

$$E_1 = \left[\sum n_i (\varepsilon_{f_i} + \varepsilon_{ch_i}) \right]_1 \quad E_2 = \left[\sum n_i (\varepsilon_{f_i} + \varepsilon_{ch_i}) \right]_2 \quad (6)$$

ε_{f_i} and ε_{ch_i} are the physical and chemical molar exergies of the i substance. The first term on the right side of (5) is associated with heat transfer to or from the system during the process

$$E_Q = \int_1^2 \left(1 - \frac{T_0}{T_F} \right) \delta Q \quad (7)$$

The second term on the right side is associated with the net useful work and can be interpreted as the exergy transfer associated with the transfer of energy by work (useful work):

$$E_W = W - P_0(V_2 - V_1) \quad (8)$$

The third term on the right side accounts for the destruction of exergy due to irreversibility within the system. The exergy destruction is related to the entropy generation by (9). This is also named *availability destruction*, *irreversibility* (I) or *lost work* (W_{dp}). The equation (9) is also known as the *Gouy-Stodola theorem*.

$$E_D = I = W_{dp} = T_0 S_{gen} \quad (9)$$

A convenient form of the exergy balance for closed systems is the rate equation (10), derived from (5). The terms are exergy fluxes, in J/s.

$$\frac{dE}{d\tau} = \left(1 - \frac{T_0}{T_F} \right) \dot{Q}_F - \left(\dot{W} - P_0 \frac{dV}{d\tau} \right) - \dot{E}_D \quad (10)$$

A2. Exergy Balance in Open Systems

In open systems there are molar flow rates as inlets \dot{n}_1 and outlets \dot{n}_2 .

$$\dot{n}_1 = (\sum \dot{n}_i)_1 \quad ; \quad \dot{n}_2 = (\sum \dot{n}_i)_2 \quad (11)$$

To extend (10) at open systems the terms accounting for exergy transfer associated to the mass exchange between the system and the environment. The equation becomes:

$$\left\{ \frac{dE}{d\tau} \right\} = \left\{ \left(1 - \frac{T_0}{T_F} \right) \dot{Q}_F - \left(\dot{W}_F - P_0 \frac{dV}{d\tau} \right) + \dot{n}_1 \varepsilon_1 - \dot{n}_2 \varepsilon_2 \right\} - \left\{ \dot{E}_D \right\}, \text{ J/s} \quad (12)$$

The continuous processes (in open systems) are usually operated in *steady state*, with properties invariable with time. The start-up and shut-down are exceptions. The balance equation of steady state open systems is obtained from (12) putting $\frac{dE}{d\tau} = 0$:

$$0 = \left(1 - \frac{T_0}{T_F} \right) \dot{Q}_F - \dot{W}_F + (\sum \dot{n}_i \varepsilon_i)_1 - (\sum \dot{n}_i \varepsilon_i)_2 - \dot{E}_D \quad (13)$$

Or:

$$\dot{E}_1 + \dot{E}_Q = \dot{E}_2 + \dot{E}_W + \dot{E}_D \quad (14)$$

The equation (14) states that the rate at which exergy is transferred into the open system ($\dot{E}_1 + \dot{E}_Q$) must exceed the rate at which exergy is transferred out ($\dot{E}_2 + \dot{E}_W$). The difference is the exergy destroyed within the system because of the irreversibility. The exergy balance is not a conservative one.

A3. Exergetic Efficiency

To define the exergetic efficiency it is necessary to identify both useful products and the inputs or resources expended to generate the products. of the system. Both are expressed in terms of exergy (\dot{E}_p, \dot{E}_{in}). Using these, the exergy balance (14) become:

$$\Sigma \dot{E}_{in} = \Sigma \dot{E}_p + \dot{E}_D \quad (15)$$

According to the second law, $\dot{E}_D \geq 0$, and the the ratio of products exergy and inputs exergy is always less than unity:

$$\frac{\Sigma \dot{E}_p}{\Sigma \dot{E}_{in}} \leq 1 \quad (16)$$

This ratio depends on the internal irreversibility of the system. That is why is also named degree of technical perfection of the system, or absolute efficiency.

$$\eta_E = \frac{\Sigma \dot{E}_p}{\Sigma \dot{E}_{in}} = 1 - \frac{\dot{E}_D}{\Sigma \dot{E}_{in}} = 1 - \frac{\Sigma \dot{I}_i}{\Sigma \dot{E}_{in}} \quad (17)$$

This is also an overall efficiency. If the system is a sequence of unit operations, the overall inefficiency ($\psi = 1 - \eta_E$) can be divided in a series :

$$\psi = 1 - \eta_E = \frac{\dot{I}_1}{\Sigma \dot{E}_{in}} + \frac{\dot{I}_2}{\Sigma \dot{E}_{in}} + \dots + \frac{\dot{I}_i}{\Sigma \dot{E}_{in}}, \text{ or } \quad \psi = \psi_1 + \psi_2 + \dots + \psi_i = \Sigma \psi_i \quad (18)$$

Where I_i is the irreversibility of the unit operation i . The equation (18) permits the evaluation of the relative contribution of each operation to the overall inefficiency of the system:

$$\varphi_i = \frac{\dot{I}_i}{\Sigma \dot{I}_i} = \frac{\psi_i}{\psi} \quad (19)$$

REFERENCES

- [1] Romero J.C. *Exergy as a global energy sustainability indicator*, Renewable. & Sustainable Energy Reviews, 33, 2014, 427- 442.
- [2] Rant Z., *Exergie, ein neues Wort fuer "technische Arbeitsfaehigkeit"*, Forschung auf dem Gebiet des ingenieurwesens, 22(1), 1956, 36- 37.
- [3] Kenney W.F., *Energy Conservation in the Process Industries*, Academic Press, Orlando, FL., 1984.
- [4] Kotas T.J., *The Exergy Method of Thermal Plant Analysis*, Butterworths, London, 1985.
- [5] Szargut J., Morris D.R., Steward F.R., *Exergy Analysis of Thermal, Chemical, and Metallurgical Processes*, Springer Verlag, 1988.
- [6] Moran M.J., *Availability Analysis: A Guide to Efficient Energy Use*, ASME Press, New York, 1989.
- [7] Siminiceanu I., *Exergy analysis of chemical processes*, Mem. Sci. Sect. Romanian Academy, 8(1) 1985, 153-159.
- [8] Jianu D., Siminiceanu I., *Exergy analysis of a chemical plant*, Rev. Chim.(Bucharest), 48(8), 1997, 713- 717.
- [9] Kirova- Yordanova Z., *Application of the exergy method to the environmental impact estimation*, Exergy, 36(6), 2011, 3733- 3744.
- [10] Denbigh K.G., *The second law efficiency of chemical processes*, Chem. Eng. Sci., 6(1), 1956, 1-9.
- [11] Rieker L., *The efficiency of energy utilization in chemical processes*, Chem. Eng. Sci., 29, 1974, 1613- 1629.
- [12] Nimkar S., Newada R., *Minimization of Exergy Losses in a Mono- high Pressure Nitric Acid Process*, International Journal of Exergy, 2014, (in press).
- [13] Winter C.-J., *Energy efficiency no: it's exergy efficiency!*, Int.Journal of Hydrogen Energy, 32(17), 2007, 4109- 4111.

ANALIZA EXERGETICĂ A SISTEMELOR INDUSTRIALE

Ilie SIMINICEANU^{1,2}

¹ Membru corespondent al Academiei de Științe Tehnice din România

² Universitatea Tehnică "Gheorghe Asachi" din Iași

Rezumat: În mod tradițional, majoritatea sistemelor industriale au fost proiectate folosind criteriile de performanță energetice bazate numai pe prima lege a termodinamicii. Analiza exergetică combină primul și al doilea principiu al termodinamicii și este un instrument puternic pentru a analiza atât cantitatea, cât și calitatea de utilizare a energiei. Astăzi, exergia este considerată cel mai bun indicator global de sustenabilitate energetică. Exergia a fost definită de Zoran Rant (1904- 1972) ca maximă " lucrul mecanic disponibil tehnic" ce se poate obține în timp ce sistemul comunică cu mediul reversibil. Primele aplicații ale analizei exergetice la procesele chimice au fost realizate de către Denbigh și Riekert. În România a fost aplicată la industria amoniacului. În septembrie 2014 ScienceDirect indica un număr de 14236 de lucrări publicate pe subiectul "analiză exergetică", 1299 înainte de 1995, cu un maxim de 1852 lucrări în 2014. O creștere constantă a numărului de lucrări relevă importanța acestui subiect. Lucrarea de față se ocupă de analiza exergetică a unei instalații de acid azotic cu oxidare a amoniacului și absorbție, la o presiune de 5 bari (5/5 proces). Acesta este un proces nou față de cele analizate de către Denbigh (1/1) și Riekert (1/5) citate mai sus. Modelul bilanțului exergetic stabilit anterior pentru sistemele chimice deschise și randamentul exergetic corespunzător au fost utilizate, împreună cu valorile măsurate ale parametrilor de funcționare (temperaturi, presiuni, debite și concentrații). Randamentul exergetic din instalația de acid azotic 5/5 este de 30.52 %, mai mare decât cel determinat de Denbigh (11.00 %) și Riekert (15.53 %), datorită îmbunătățirilor tehnice. Exergia totală pierdută și distrasă de ireversibilitate a fost de 5156 kW, față de intrarea de 7421 kW. Cele mai mari contribuții le-au avut reactorul de oxidare a amoniacului (44.97 %), absorbția - coloana de reacție (20.17 %), aburul peste încălzitor (19.05 %), preîncălzitorul de apă (5.77 %) și turbina (4.50 %). Modul de a îmbunătăți randamentul acestor operațiuni este de asemenea discutat în lucrare.