

# Thermoeconomical analysis of an endoreversible chemical engine model with a diffusive transport law of particles

M A Barranco<sup>2</sup>, A Ocampo<sup>2</sup> J. C. Pacheco<sup>2</sup> and F Angulo<sup>2</sup>

<sup>1</sup>Departamento de Formación Básica, Escuela Superior de Cómputo del Instituto Politécnico Nacional, Av. Juan de Dios Bátiz s/n. UP Zacatenco, CP 07738, D. F., México. *mbarrancoj@ipn.mx*,

<sup>2</sup>Departamento de Física, Escuela Superior de Física y Matemáticas del Instituto Politécnico Nacional, Edif. 9, 2° Piso, UP Zacatenco CP 07738, D.F., México.

E-mail: *aocampog@esfm.ipn.mx*, *jcpacheco@esfm.ipn.mx*, *angulo@esfm.ipn.mx*

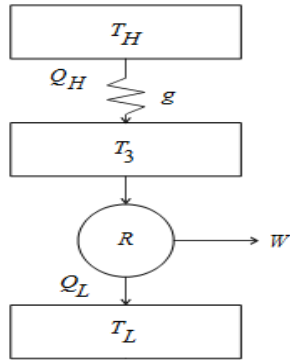
**Abstract.** In 1995, De Vos introduced a thermoeconomical analysis for heat engines working in finite time. This analysis was made by the maximization of a benefit function defined as the ratio of the power output and the total costs which are associated to the investment and the fuel consumption. The De Vos methodology has been applied to several heat engine models working at different regimes of performance. In the present work we apply this methodology to a simple model of a chemical engine which works between two reservoirs of constant chemical potential. In this work we take into account a diffusive transport law of particles. From the optimization of the benefit chemical functions defined as the ratio of some characteristic function (power output, efficient power and ecological function) and the total cost involved in the performance of the chemical engine, we obtain the optimal chemical efficiencies under different regimes of performance in an analogous way to the thermo-economic method proposed by De Vos.

## 1. Introduction

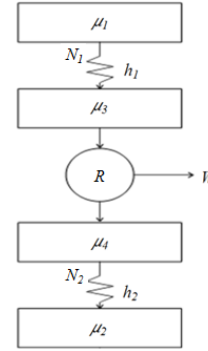
In 1995 [1], De Vos introduced a thermoeconomical analysis of an irreversible heat engine model, the so-called Novikov plant model (see Figure 1) [2], in terms of the maximization of an objective function defined by the ratio of the power output and the running costs of the plant exploitation. De Vos [1] assumed that the running costs of the plant consist of two parts: a capital cost that is proportional to the investment and, therefore, to the size of the plant and a fuel cost that is proportional to the fuel consumption. De Vos [1] showed how the optimal efficiency,  $\eta_{opt}$  (in the economical sense) smoothly increases from the maximum-power point (Curzon-Ahlborn efficiency,  $\eta_{CA}$  [3]) corresponding to energy sources where the investment is the preponderant cost up to the Carnot value (Carnot efficiency,  $\eta_C$ ), that is, for energy sources where the fuel is the predominant cost when the heat fluxes in the Novikov model are given by a linear Newtonian heat transfer law; that is,  $\eta_{MP} < \eta_{opt} < \eta_C$ , where the subscripts  $MP$ ,  $opt$  and  $C$  mean maximum power, optimal efficiency and Carnot respectively. De Vos [1] found for the Novikov's model that  $\eta_{opt}$  is given by,

$$\eta_{opt}(\tau, f) = 1 - \frac{f}{2} \tau - \frac{\sqrt{4(1-f)\tau + f^2\tau^2}}{2}, \quad (1)$$

where  $f$  is the fractional fuel cost (see Table 1 of the Ref. [1]), which is defined as the ratio of the cost of the fuel consumption and the running costs of the power plant;  $\tau = T_L/T_H$  with  $T_H$  and  $T_L$  the temperatures of the hot and cold thermal reservoirs respectively (see Fig. 1). Later, Barranco-Jiménez and Angulo-Brown [4, 5] also studied the Novikov engine model following the thermoeconomical approach used by De Vos, but by means of the so-called ecological optimization criterion. The ecological optimization criterion consists in maximizing the well known ecological function [6, 7] defined as  $E = W - T_L\sigma$ , where  $W$  is the plant's power output and  $\sigma$  is the total entropy production of the endoreversible power plant model. Barranco-Jiménez and Angulo-Brown [4, 5] also obtained an optimal efficiency  $\eta_{opt}^E$  between  $\eta_{MP}$  and  $\eta_C$  that drastically reduces the entropy production of the engine. Besides the optimal efficiency satisfy the following inequality  $\eta_{MP} < \eta_{opt} < \eta_{opt}^E < \eta_C$  [8].



**Figure 1.** Novikov's model for a thermal power plant.



**Figure 2.** Endoreversible chemical engine.

The concept of heat engine working between two thermal reservoirs has been extended to chemical engines working between two reservoirs of constant chemical potential  $\mu$  [9]. This model of chemical engine has been studied under the methodology of finite-time thermodynamics (FTT) [9-12]. Some authors [13] have considered that these chemical engine models can have practical value for many devices such as chemically reactive devices, mass exchangers, photochemical cells and solid-state devices. Recently, Barranco-Jiménez et al. [14] also studied the thermoeconomics of an endoreversible chemical engine model by applying the De Vos methodology. In that study, they also take into account a linear mass transfer law that comes from the linear irreversible thermodynamics [9, 13]. Besides, in their study they consider three different regimes of performance: maximum power output [3], maximum efficient power [15-17] and maximum ecological function [6]. In the present work we also study the thermoeconomics of an endoreversible chemical engine but taking into account a diffusive transport law of particles. From the optimization of the benefit chemical functions defined as the ratio of a characteristic function (power output, efficient power and ecological function) and the total cost involved in the performance of the chemical engine, we obtain the optimal chemical efficiencies under different regimes of performance by using the De Vos methodology.

## 2. Thermoeconomical optimization of an endoreversible chemical engine.

The schematic diagram of an isothermal chemical engine model is shown in Figure 2. The two mass reservoirs associated to the chemical engine have chemical potentials  $\mu_1$  and  $\mu_2$ . The configuration of the chemical engine is analogous to that of thermal engines with heat fluxes. The chemical engine receives the mass flux  $N_1$  at chemical potential  $\mu_3$  from the high chemical potential  $\mu_1$  in time  $t_1$  and rejects the mass flux  $N_2$  at chemical potential  $\mu_4$  to the low chemical potential  $\mu_2$  in time  $t_2$ . In his

1991 paper [9] De Vos studied a chemical reactor by means of a Fick-type particle diffusive law. Following Fig. 2 the fluxes  $N_1$  y  $N_2$  are given by,

$$N_1 = h_1(n_1 - n_3), \quad (2)$$

$$N_2 = h_2(n_4 - n_2), \quad (3)$$

where  $h_1$  y  $h_2$  are particle conductances also called coefficients of diffusivity, and  $n_i$  ( $i=1, 2, 3, 4$ ) are the particle concentrations per unit volume, and they are related with the chemical potentials by means of,

$$\mu_i = \mu_0 + kT \ln \frac{n_i}{n_0}, \quad (4)$$

where  $\mu_0$  denotes the chemical potential at normalized concentration  $n_0$ , being  $k$  the Boltzmann constant. From mass conservation we have,

$$N_1 = N_2 = N. \quad (5)$$

Applying the first law of thermodynamics to the model of Figure 2 we obtain,

$$\mu_4 N + W - \mu_3 N = 0. \quad (6)$$

By combining Eqs. (4) and (6) we get,

$$\xi = \mu_3 - \mu_4 = \xi_0 + kT \ln \left( \frac{n_3}{n_4} \right), \quad (7)$$

being  $\xi$  the work production per mole of fuel, which is given by  $\xi = W/N$ , and from Eq. (4) immediately we obtain

$$\xi_0 = \mu_{03} - \mu_{04} = \mu_{01} - \mu_{02}, \quad (8)$$

by using Eqs. (2), (3) and (5) we get,

$$h_1(n_1 - n_3) = h_2(n_4 - n_2), \quad (9)$$

by solving Eqs. (7) and (9) for the two unknown concentrations  $n_3$  and  $n_4$  we obtain [9],

$$n_3 = \frac{h_1 n_1 + h_2 n_2}{h_1 + h_2 \exp\left(-\frac{\xi - \xi_0}{kT}\right)}, \quad (10)$$

$$n_4 = \frac{h_1 n_1 + h_2 n_2}{h_2 + h_1 \exp\left(\frac{\xi - \xi_0}{kT}\right)}. \quad (11)$$

By substituting Eq. (9) into Eq. (2) we have,

$$N = \frac{n_1 - n_2 \exp\left(\frac{\xi - \xi_0}{kT}\right)}{\frac{1}{h_1} + \frac{1}{h_2} \exp\left(\frac{\xi - \xi_0}{kT}\right)}. \quad (12)$$

From Eq. (12) and by using the definition of  $\xi$  we obtain,

$$W = \xi \frac{n_1 - n_2 \exp\left(\frac{\xi - \xi_0}{kT}\right)}{\frac{1}{h_1} + \frac{1}{h_2} \exp\left(\frac{\xi - \xi_0}{kT}\right)}. \quad (13)$$

On the other hand, when we apply the second law of thermodynamics to Fig. 2, the rate of entropy production of the chemical engine is given by [9],

$$\sigma = (\xi_C - \xi) \frac{N}{T}, \quad (14)$$

where  $\xi_C$  is the “Carnot” chemical efficiency and by using Eq. (4) it results [9],

$$\xi_C = \mu_1 - \mu_2 = \xi_0 + kT \ln \left( \frac{n_1}{n_2} \right), \quad (15)$$

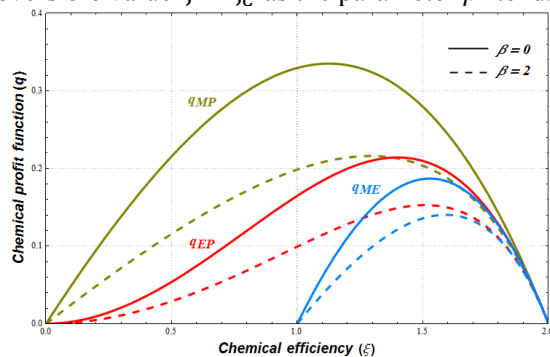
by substituting Eq. (12) into Eq. (14) we arrive to,

$$\sigma = \left[ \frac{\xi_0}{T} + k \ln \left( \frac{n_1}{n_2} \right) - \frac{\xi}{T} \right] \frac{n_1 - n_2 \exp \left( \frac{\xi - \xi_0}{kT} \right)}{\frac{1}{h_1} + \frac{1}{h_2} \exp \left( \frac{\xi - \xi_0}{kT} \right)}. \quad (16)$$

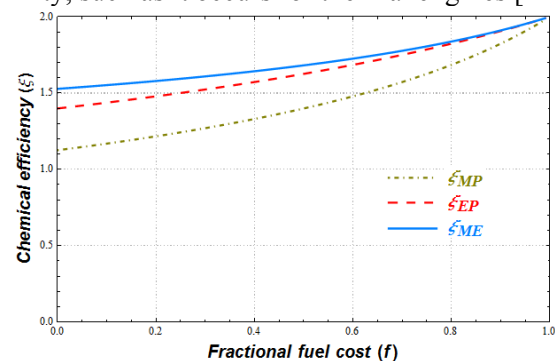
For our thermoeconomical optimization, we apply the De Vos methodology to the chemical engine model by maximizing three benefit chemical functions defined by the ratio of the corresponding characteristic function (Power Output (MP), [1], Efficient Power (EP), [15, 16] and Ecological Function (ME) [6]) and the total costs involved in the performance of the chemical engine, that is,  $q_{MP} = \frac{W}{C}$ ,  $q_{EP} = \frac{\xi W}{C}$  and  $q_{ME} = \frac{W - T\sigma}{C}$  [14]. Besides in the maximization of the benefit chemical functions, the total costs  $C$  are taken as  $C = C_{inv} + C_{fuel} = aN_{max} + bN$ , where the proportionality constants  $a$  and  $b$  have units of  $\$ \cdot time$  ( $\$$ :currency) and  $N_{max}$  is the maximum mass transfer without supplying chemical work. To illustrate the mathematical form for the benefit chemical functions we only show the case of  $q_{MP}$ ,

$$q_{MP} = \frac{\xi n_1 h_1 \frac{1 - \exp \left( \frac{\xi - \xi_C}{kT} \right)}{1 + n \exp \left( \frac{\xi - \xi_C}{kT} \right)}}{\xi_C n_1 h_1 \frac{1 - \exp \left( \frac{-\xi_C}{kT} \right)}{1 + n \exp \left( \frac{-\xi_C}{kT} \right)} + \beta n_1 h_1 \frac{1 - \exp \left( \frac{\xi - \xi_C}{kT} \right)}{1 + n \exp \left( \frac{\xi - \xi_C}{kT} \right)}}. \quad (17)$$

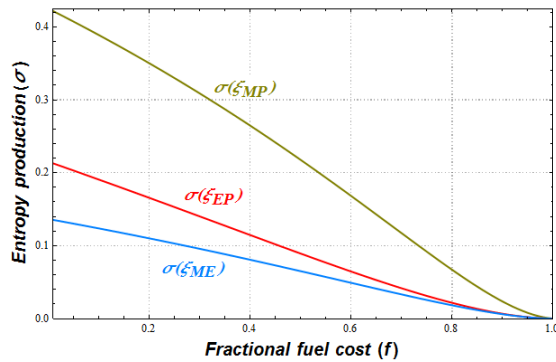
We see that the curve of  $q_{MP}$  presents a maximum point  $\xi^*$  between 0 and  $\xi_C$ . The maximization condition  $dq_{MP}/d\xi = 0$  results in a transcendental equation. The same occur for  $q_{EP}$  and  $q_{ME}$  (see Fig. 3). Figure 3 shows the behavior of the three profit chemical functions and we can observe that there exists an optimal chemical efficiency value which depends on the parameter  $\beta = b/a$  and the optimum value of the chemical efficiency  $\xi^*$ . We can also observe that the maximum of benefits tends to the reversible value  $\xi = \xi_C$  as the parameter  $\beta$  tends to infinity, such as it occurs for thermal engines [1-4].



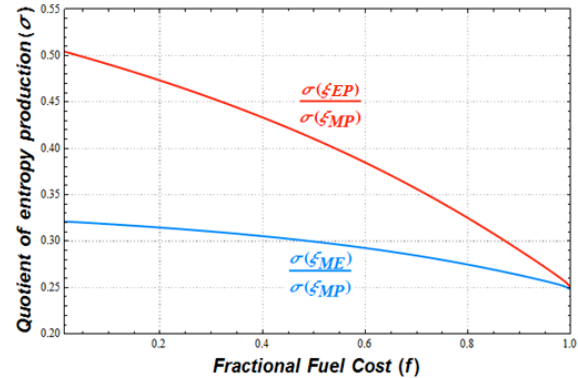
**Figure 3.** Comparison between the three chemical benefit functions versus chemical efficiency for two values of  $\beta$ .



**Figure 4.** Optimal efficiencies for ecological regime, efficient power and maximum power output conditions.



**Figure 5.** Entropy production under the three regimes of performance vs. fractional fuel cost



**Figure 6.** Ratio of entropy production vs. fractional fuel cost.

The optimal chemical efficiencies are obtained in terms of the dimensionless parameter  $\beta$  but now with a chemical meaning. Also in these cases we can define a fractional cost defined as the ratio between the reactants cost and the total costs of the plant, that is,

$$f = \frac{bN}{aN_{max} + bN} = \frac{\beta N}{N_{max} + \beta N}. \quad (18)$$

In Figure 4, we show the optimal efficiencies under the three regimes of performance. As it is shown in these figures the three optimal efficiencies smoothly increase from the maximum efficient point (in each regime), corresponding to energy sources where the investment is the preponderant cost up to the “Carnot” chemical efficiency ( $\xi_c$ ), that is, for energy sources where the reactants are the predominant cost [1], and we can also observe that for all the values of the fractional cost, the optimal efficiencies satisfy the following inequality,

$$\frac{\xi_c}{2} < \xi_{MP}^* < \xi_{EP}^* < \xi_{ME}^* < \xi_c. \quad (19)$$

Finally, we can calculate the total entropy production and the power output under the three regimes of performance. In Fig. 5 we see how the inequality  $\sigma_{MP}^* > \sigma_{EP}^* > \sigma_{ME}^*$  is hold [6, 7, 14]. In Fig. 6, we can see how the ME-regime produces less entropy than the other two regimes.

### 3. Concluding Remarks

In the present work, we applied the De Vos methodology to an endoreversible chemical engine model, i. e., an engine operating between two reservoirs of constant chemical potential. In our chemical engine model we take into account a diffusive transport law of particles. From the maximization of chemical profit-functions defined in terms of some model characteristic functions (power output, efficient power and ecological function) and the costs related to investment and reactants consumption, we obtain the optimum efficiencies for this model under different performance regimes. Besides, we analyze both, the effect on the reduction of power output and the reduction in the total entropy production under the three considered regimes of performance. The extension of thermoeconomic studies from heat engines to chemical engines can be useful to analyze some aspects of biochemical systems, such as photosynthetic processes.

### Acknowledgments

This work was supported in part by CONACYT, COFAA and EDI-IPN-México.

- [1] De Vos A 1995 *Endoreversible thermoeconomics. Energy. Convers. Management.*;36:(1)1-5
- [2] Novikov I I 1957 *The efficiency of atomic power stations (a review) Atomimaya Energiya* **3** 409 (English translation 1958. *Nuclear Energy* 7 125)

- [3] Curzon F. and Ahlborn B 1975 *Efficiency of a Carnot engine at maximum power output*. Am. J. Phys.;43:22-24
- [4] Barranco M and Angulo F 2007 “*Thermoeconomic optimization of a Novikov power plant model under maximum ecological conditions*” J. of the Energy Inst. 80:2(1-4):96-104
- [5] Barranco M 2009 “Finite-time thermoeconomic optimization of a non endoreversible heat engine”, Rev. Mex. Fis. 55 (3) 211-220
- [6] Angulo F 1991 *An ecological optimization criterion for finite-time heat engines*. J. Appl. Phys. 69:7465-7469
- [7] Arias L and Angulo F 2001 Reply to “Comment on A general property of endoreversible thermal engines” [J. Appl. Phys. 89, 1518]
- [8] M. A. Barranco-Jiménez, N. Sánchez-Salas, F. Angulo-Brown, “*On the optimum operation conditions of an endoreversible heat engine with different heat transfer laws in the thermal couplings*”, Rev. Mex. Fis. 54 (4), 284-292
- [9] De Vos A, Endoreversible 1992 *Thermodynamics of a solar energy conversion*. Oxford University: Oxford University Press
- [10] Chen L, Sun F and Wu C 1998 *Performance of chemical engines with a mass leak*, J. Phys. D: Appl. Phys. 31, 1596-1600
- [11] Chen L, Sun F, Wu C and Yu J 1997 *Performance characteristic of isothermal chemical engines*, Energy. Convers. Mgmt, 38 (18), 1841-1846
- [12] Xia S, Chen L and Sun F 2009 *Optimal configuration of a finite mass reservoir isothermal chemical engine for maximum work output with linear mass transfer law*. Rev. Mex. Fis. 55 (5), 399-408
- [13] Xia S, Chen L and Sun F 2010 *Optimal performance of a generalized irreversible chemical engine with diffusive mass transfer law*, Mathematical and Computer Modelling, 51, 127-136
- [14] Barranco M. A., Ocampo A and Angulo F 2016 *Thermoeconomical optimization for an endoreversible chemical engine model*. Proceedings of ECOS2014, Portoroz Eslovenia, June 19-23
- [15] Pacheco J, Angulo F and Barranco M 20015 “*Thermoeconomical analysis of a non-endoreversible Novikov power plant model under different regimes of performance*”, J. Phys.: Conf. Ser. 582 012050
- [16] Yilmaz T 2006 *A new performance criterion for heat engine: efficient power*. J. Energy Inst. 79(1):38-41
- [17] Arias L, Barranco M and Angulo F 2009 “*Comparison between two ecological-type modes of performance for a simple energy converter*”, Journal of the Energy Institute, 82 (3) 193-197