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Non-Instantaneous Adiabats in Finite Time

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1. Introduction

Since the pioneer paper of Curzon and Ahlborn (1975), the so called finite time thermodynamics has been in development. Curzon and Ahlborn proposed a model of thermal engine called endoreversible cycle or Curzon and Ahlborn cycle, shown in Figure 1, with the so called Curzon-Ahlborn-Novikov efficiency,

\[ \eta_{CAN} = 1 - \sqrt{\frac{T_C}{T_H}}, \]

where \( T_C \) is the cold reservoir temperature and \( T_H \) is the hot reservoir temperature. This endoreversible cycle is an engine in which the endoreversibility condition, \( Q_H / T_{HV} = Q_C / T_{CW} \), is fulfilled and the entropy production during the exchange of heat, \( Q_H \) and \( Q_C \), between the system and its reservoirs of heat is only taken into account. The temperatures of working substance are \( T_{HV} \) and \( T_{CW} \). The relation between these temperatures in the cycle is \( T_C < T_{CW} < T_{HV} < T_H \).

Fig. 1. Curzon and Ahlborn cycle in the entropy \( S \) vs temperature \( T \) plane.
As we can see, Carnot efficiency, $\eta_C$, is obtained when the temperatures of reservoirs are the same as engine temperatures, which means $T_{H,V} = T_H$ and $T_C = T_{C,V}$ in Figure 1, namely,

$$\eta_C = 1 - \frac{T_C}{T_H} = 1 - \frac{T_{C,V}}{T_{CH}}$$  \hspace{1cm} (2)

Equation (1) was previously advanced by Chambadal (1957) and Novikov (1958), among others, and has been recovered by some procedures (Salamon, et al., 1976; Rubin, 1979a, 1979b, 1980; Bejan, 1996; Gutkowicz-Krusin et al., 1978 among others). Particularly, the optimal configuration of heat engines was studied (Rubin, 1979a), and it was introduced a procedure in which the power output of cycle is taken as a function of the compression ratio by using the parameter

$$\lambda \sim \left[ \ln V_{\text{max}} - \ln V_{\text{min}} \right]^{-1},$$

where $V_{\text{max}}$ and $V_{\text{min}}$ are the maximum and the minimum volumes spanned in the cycle, respectively (Gutkowicz-Krusin et al., 1978). More recently, this subject has been also studied by other authors (Badescu, 2004; Amelkin, et al., 2004, 2005; Song et al., 2006, 2007). Even more Angulo-Brown (1991) introduced an optimization criterion of merit for the Curzon and Ahlborn cycle taking into account entropy production, the ecological criterion, through the function

$$E = P - T_C \sigma,$$

where $P$ is the power output, $T_C$ is the temperature of cold reservoir and $\sigma$ is the total entropy production. The function in (3) is known as ecological function, and at maximum of this function the efficiency of Curzon and Ahlborn cycle can be written as,

$$\eta_E = 1 - \sqrt{\left( e^2 + e \right) / 2}.$$  \hspace{1cm} (4)

A comparison of values obtained with the previous expressions of efficiency, for some plants reported in the literature of finite time thermodynamics, is shown in Table 1. Notice that the ecological criterion proposed by Angulo-Brown for finite-time Carnot heat engines, Equation (3), represents a compromise between the high power output $P$ and a loss power output, $T_C \sigma$. However Yan (1993) showed that it might be more reasonable to use $E_0 = P - T_0 \sigma$ if the cold reservoir temperature $T_C$ is not equal to the environments temperature $T_0$ because in the definition of $E$ two different quantities, exergy output, $P$, and a non-exergy $T_C \sigma$, were compared together. The criterion with function $E_0$ is more reasonable than that presented by Angulo-Brown. Nevertheless, since $E_0 \to E$ when $T_0 \to T_C$, it can be used as the optimization of $E$ without loss of generality.

Recently, following the procedure of Gutkowicz-Krusin et al (1978) the form of the ecological function and its efficiency was found using the Newton heat transfer law and ideal gas as working substance (Ladino-Luna & de la Selva, 2000), and using Dulong-Petit heat transfer law for ideal gas as working substance (Ladino-Luna,2003).

It is important to remark that Curzon and Ahlborn efficiency is an adequate approximation for conventional power plants, and ecological efficiency is the adequate approximation for modern power plants (nuclear and others), as it is shown in Table 1. On other hand, in nature there are no endoreversible engines. Thus, some authors have analyzed the non-endoreversible Curzon and Ahlborn cycle. Ibrahim et al. (1991), and Wu and Kiang (1992) proposal include a non-endoreversibility parameter to take into account
Table 1. Values of different efficiency expressions for the cycle in Figure 1. $T$ is in Kelvin scale.

<table>
<thead>
<tr>
<th>Plant</th>
<th>$T_C/T_H$</th>
<th>$\eta_C$</th>
<th>$\eta_{CAN}$</th>
<th>$\eta_{E}$</th>
<th>$\eta_{obs}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>West Thurrock (coal fired steam plant), U K</td>
<td>298/838</td>
<td>0.64439</td>
<td>0.40367</td>
<td>0.50905</td>
<td>0.360</td>
</tr>
<tr>
<td>Lardarello (geothermal steam plant), Italy</td>
<td>353/523</td>
<td>0.32505</td>
<td>0.17845</td>
<td>0.24818</td>
<td>0.160</td>
</tr>
<tr>
<td>Central steam power station, U K</td>
<td>298/698</td>
<td>0.57307</td>
<td>0.3466</td>
<td>0.44809</td>
<td>0.280</td>
</tr>
<tr>
<td>Steam power plant, U S A</td>
<td>298/923</td>
<td>0.67714</td>
<td>0.43179</td>
<td>0.55447</td>
<td>0.400</td>
</tr>
<tr>
<td>Combined-cycle (steam and mercury), U S A</td>
<td>298/783</td>
<td>0.61941</td>
<td>0.38308</td>
<td>0.48744</td>
<td>0.340</td>
</tr>
<tr>
<td>Doel 4 (nuclear pressurized water reactor), Belgium</td>
<td>283/566</td>
<td>0.50000</td>
<td>0.29289</td>
<td>0.38763</td>
<td>0.350</td>
</tr>
<tr>
<td>Almaraz II (nuclear pressurized water reactor), Spain</td>
<td>290/600</td>
<td>0.51667</td>
<td>0.30478</td>
<td>0.40127</td>
<td>0.345</td>
</tr>
<tr>
<td>Sizewell B (nuclear pressurized water reactor), U K</td>
<td>288/581</td>
<td>0.50430</td>
<td>0.29594</td>
<td>0.39114</td>
<td>0.363</td>
</tr>
<tr>
<td>Cofrentes (nuclear boiling water reactor), Spain</td>
<td>289/562</td>
<td>0.48577</td>
<td>0.28290</td>
<td>0.37603</td>
<td>0.340</td>
</tr>
<tr>
<td>Heysham (nuclear advanced gas cooled reactor), U K</td>
<td>288/727</td>
<td>0.60385</td>
<td>0.37060</td>
<td>0.47413</td>
<td>0.400</td>
</tr>
</tbody>
</table>

where $\Delta S_C$ is the entropy change during heat exchange from the engine to the cold reservoir, and $\Delta S_H$ is the entropy change during heat exchange from the hot reservoir to the engine. Chen et al. (2004, 2006) carried out the ecological optimization for generalized irreversible Carnot engine with heat resistance, heat leakage and internal irreversibility for newtonian heat transfer law. Zhu et al. (2003) used a generalized convective heat transfer law $Q \propto (\Delta T)^n$, and generalized radiative heat transfer law $Q \propto (\Delta T^3)$. More recently the ecological optimization for generalized irreversible universal heat engine, including Diesel, Otto, Bryton Atkinson, Dual and Miller cycles, with heat resistance, heat leakage and internal irreversibility was carried out for newtonian heat transfer law (Chen et al., 2007). The non-endoreversible Curzon and Ahlborn cycle model is shown in Figure 2. The efficiency of Curzon and Ahlborn cycle using the parameter in Equation (5), at maximum power output was found as (Chen, 1994, 1996),

$$\eta_m = 1 - \sqrt{I_S \epsilon}, \quad I_S > 1.$$  (6)

On other hand, Angulo-Brown et al (1999) showed that a general property of endoreversible Curzon and Ahlborn cycle demonstrated previously (Árias-Hernández & Angulo-Brown, 1997) can be extended for a non-endoreversible Curzon and Ahlborn cycle. Besides, Velasco et al. (2000) follow the idea in Chen (1994, 1996), and they found expressions to measure possible reductions of non-desired effects in heat engines operation. They pointed out that $I_S$ is not depending of $\epsilon$ and re-wrote Equation (6) as,
\[ \eta_m = 1 - \sqrt{e / I}, \quad I = I_{S}, \quad 0 < I < 1. \quad (7) \]

Even more, Angulo-Brown et al. (2002) applied variational calculus to show that both the saving function (Velasco et al., 2000) and a modified ecological criterion are equivalent. These previous results have been found assuming an ideal gas as working fluid. However, in a real context, a thermal engine works with a non-ideal gas. The performance of a finite time cycle with a van der Waals gas as working fluid was analyzed among others by Agrawal & Menon (1990), and more recently by Ladino-Luna (2005).

In the present work it is shown that some of internal irreversibilities can be taken into account for a more general expression of both power output and ecological function, with a non-linear heat transfer law like \[ \frac{dQ}{dt} \propto (\Delta T)^k \], assuming the Curzon and Ahlborn cycle with non-instantaneous adiabats. Approximate efficiencies curves at maximum power output and at maximum ecological function are shown for \( k = \frac{5}{3} \), that is in case of the Dulong and Petit heat transfer law. Comparative tables of values of efficiencies are shown for certain power plants reported in some papers, (Árias-Hernández & Angulo-Brown, 1997; Velasco et al., 2000 and more recently Ladino-Luna, 2008). The cycle analysis shall be treated assuming both ideal gas and van der Waals gas as working fluids. Also, we show that power output and ecological function have a similar property when the compression ratio is taking into account, e.g. the efficiency obtained at maximum of each of objective function with the definition \( e = T_C / T_H \) is a bound for efficiencies, when an engine is modeled as a Curzon and Ahlborn cycle working at maximum of each objective function and the time of all the processes in the cycle is took into account (Ladino-Luna & de la Selva, 2000; Ladino Luna, 2003). All of quantities have been taken in the International Measurement System.
2. Non-instantaneous adiabats with Newton’s heat transfer law

From classical thermodynamics, the efficiency of a reversible thermal engine working between two temperatures $T_{HW} > T_{CW}$ is known when heat exchanged is also known. In this description, the temperatures of working gas in the isothermal processes, $T_{HW}$ and $T_{CW}$, are assumed to be the same as that of the corresponding reservoirs. As a consequence the process associated with the heat transfer between the engine and the reservoirs is ignored. The upper limit of the efficiency of any heat engine corresponds to the Carnot cycle, $\eta_C$, in which the temperatures of the reservoirs are the same as the temperatures of the heat engine in Figure 1, as it was shown in Equation (2). Thus, the definition of efficiency of an engine working in cycles leads to the Carnot efficiency, fulfilling,

$$\frac{Q_H - Q_C}{Q_H} \leq 1 - \frac{T_{CW}}{T_{HW}}$$

(8)

It is important to note that the following expressions, with the change $\varepsilon = T_C / T_H$, Carnot efficiency $\eta_C = 1 - \varepsilon$, Curzon and Ahlborn-Novikov efficiency $\eta_{C\!A\!N} = 1 - \sqrt{\varepsilon}$ and ecological efficiency $\eta_E = 1 - \sqrt{(\varepsilon^2 + \varepsilon) / 2}$, and using the Newton heat transfer law, appear as a function of $\varepsilon$, so they can be written in general as,

$$\eta = 1 - z(\varepsilon),$$

(9)

Thus, the problem of finding the efficiency of a heat engine modeled as a Curzon and Ahlborn cycle, and using either of two alternatives, maximizing power output or maximizing ecological function, becomes the problem of finding a function $z = z(\varepsilon)$, as complicated or simple as to allow the heat transfer law being used and the chosen procedure. So, substituting $z = z(\varepsilon)$ in expression (9) the efficiency is obtained as

$$\eta = \eta(\varepsilon).$$

(10)

So we can use the Newton’s heat transfer law, and also we can assume the same thermal conductance $\alpha$ in two isothermal processes of Curzon and Ahlborn cycle. The heat exchanged between the engine and its surroundings can be expressed as,

$$\frac{dQ_H}{dt} = \alpha(T_H - T_{HW}) \quad \text{and} \quad \frac{dQ_H}{dt} = \alpha(T_C - T_{CW}).$$

(11)

2.1 The Gutkowics-Krusin, Procaccia and Ross model

With the previous ideas, to make the present paper self-contained we include in this section a brief explanation and some results of model used by Gutkowicz-Krusin et al (1978), and others that we need for our present purposes. In their model Gutkowicz-Krusin et al. consider a working substance inside of a cylinder with a movable piston as engine, and also they considered an ideal gas as working fluid, contained in the cylinder and the mass of piston not negligible. The inertia of the movable piston does not affect the endoreversible character of Curzon and Ahlborn cycle to consider the expansion of gas, and because the volume occupied by the gas in the expansion and compression can be written as
\[ V = l \cdot A, \quad (12) \]

where \( V \) is the volume occupied by the gas, \( A \) is the cross section area (constant) of the cylinder and \( l \) is the distance traveled by the piston in the expansion or compression of gas. The acceleration of the piston during the processes is

\[ \frac{d^2l}{dt^2} = \frac{1}{A} \frac{d^2V}{dt^2}, \quad (13) \]

so that, from the pressure definition,

\[ \text{pressure} = \frac{\text{force}}{\text{area}}, \quad (14) \]

and with the Newton’s second law, namely \( \text{force} = (\text{mass}) \cdot (\text{acceleration}) \), we can write,

\[ \frac{1}{A} \left( m \frac{d^2l}{dt^2} \right) = \frac{\text{force}}{\text{area}} = \text{pressure}. \quad (15) \]

For the gas+piston system, the difference in internal and external pressures is expressed by

\[ p - p_{\text{ext}} = \frac{m}{A} \frac{d^2V}{dt^2}. \quad (16) \]

On other hand, conservation of energy law of the system can be written as

\[ \frac{dU}{dt} = \frac{dQ}{dt} - p_{\text{ext}} \frac{dV}{dt} - \frac{m}{A} \frac{d^2V}{dt^2}, \quad (17) \]

where the last term represents the power output during the movement of piston to take volumen \( V \). Substituting (16) in (17) it is obtain

\[ \frac{dU}{dt} = \frac{dQ}{dt} - p_{\text{ext}} \frac{dV}{dt} - (p - p_{\text{ext}}) \frac{dV}{dt} \quad \delta \quad \frac{dU}{dt} = \frac{dQ}{dt} - p \frac{dV}{dt}, \quad (18) \]

which means that the system is in mechanical equilibrium with its surroundings. Now, we can find the form of time for each process using the Newton’s heat transfer law, Equation (11). For isothermal processes, using an ideal gas we have \( U = U(T) = \text{constant} \), indicating that (18) is reduced to the expression,

\[ \frac{dQ}{dt} = p \frac{dV}{dt}. \quad (19) \]

Due to the equation of state for ideal gas, (19) can be written as

\[ \frac{dQ}{dt} = \frac{RT}{V} \frac{dV}{dt} = RT \frac{d}{dt} (\ln V); \quad (20) \]

The power, defined by the quotient of the total work output \( W \) and the total time \( t_{\text{tot}} \) is as,
\[ P = \frac{W}{t_{\text{tot}}} = \frac{\alpha(T_{\text{HV}} - T_{\text{CW}}) \left( \ln \frac{V_1}{V_2} + \frac{1}{\gamma - 1} \ln \frac{T_{\text{CW}}}{T_{\text{HW}}} \right)}{t_{\text{is}} \left( \frac{1}{\gamma - 1} + \frac{\gamma}{\gamma - 1} \right) \ln \frac{V_3}{V_1}}. \]  

(21)

\( \alpha \) is the thermal conductance, \( \gamma = C_p / C_v \); \( t_{\text{tot}} \) is the cycle period and the adiabatic processes are not instantaneous. In fact,

\[ t_{\text{TOT}} = t_1 + t_2 + t_3 + t_4 \]  

(22)

where the times for the isothermal processes have been found to be,

\[ t_1 = \frac{RT_{\text{HV}}}{\alpha(T_H - T_{\text{HV}})} \ln \frac{V_2}{V_1} \quad \text{and} \quad t_3 = \frac{RT_{\text{CW}}}{\alpha(T_C - T_{\text{CW}})} \ln \frac{V_4}{V_3}, \]

(23)

and the times for the adiabatic processes have been assumed to be:

\[ t_2 = f_1 \ln \frac{V_3}{V_2} \quad \text{and} \quad t_4 = f_2 \ln \frac{V_4}{V_3}, \]

(24)

with

\[ f_1 = \frac{RT_{\text{HV}}}{\alpha(T_H - T_{\text{HV}})} \quad \text{and} \quad f_2 = \frac{RT_{\text{CW}}}{\alpha(T_C - T_{\text{CW}})}, \]

(25)

where \( R \) is the general constant of gases. The heat flows, \( Q_H \) and \( Q_C \) are assumed to be given by Newton’s heat transfer law, as (11). The power output is written in terms of the variables \( u = T_{\text{HV}} / T_H \) and \( z = T_{\text{CW}} / T_{\text{HV}} \) from which we obtain \( P = P(u, z) \) as,

\[ P = \frac{\alpha T_H (1 - z) \left[ 1 + \lambda \ln z \right]}{1 - z + \frac{z}{\gamma - z}}, \]

(26)

and its maximization conditions \( \partial P / \partial u = 0 \) and \( \partial P / \partial z = 0 \) allow to obtain

\[ u = \frac{z + \epsilon}{2z}, \]

(27)

and

\[ (z^2 - \epsilon)(1 + \lambda \ln z) = \lambda(z - \epsilon)(1 - z); \]

(28)

where \( \lambda \) represents the external parameter,

\[ \lambda = \frac{1}{(\gamma - 1) \ln(V_3 / V_1)} \]

(29)

meaning that

\[ P_{\text{max}} = P_{\text{max}}(u(z), z), \]

(30)
that is \( P_{\text{max}} \) is a projection on the \((z, P)\) plane. It is also found that at the maximum power condition \( z \) is given by a power series in \( \lambda \):

\[
z_{p} = \sqrt{e} + \frac{1}{4}(1 - \sqrt{e})^2 \lambda + \frac{1}{4}(1 - \sqrt{e})^2 \left[ (1 - \sqrt{e})^2 / 2 \sqrt{e} - \ln e \right] \lambda^2 + O(\lambda^3)
\]

(31)

Upon substituting Equation (31) in Equation (9) and because the terms in the series (31) are positive, an upper bound for the efficiency is obtained when \( \lambda = 0 \), i.e. when the engine size goes towards infinity, it is the following one:

\[
\eta_{\text{max}} = 1 - z_{p}(\lambda = 0) = \eta_{\text{CAN}}
\]

(32)

In the next section we construct the equation analogous to (31) for the ecological function following the Gutkowicz-Krusin, Procaccia and Ross model outlined here.

2.2 The ecological function

In the ecological function, Equation (3), we take \( P \) from Equation (26) and the entropy production term \( \sigma \) as \( \sigma = \Delta S / t_{\text{tot}} \), where \( \Delta S \) represents the entropy change caused at the isothermal processes because of the heat transfers Equation (11),

\[
\sigma = \frac{1}{t_{\text{tot}}} \left( \frac{Q_{C}}{T_{C}} - \frac{Q_{H}}{T_{H}} \right).
\]

(33)

\( t_{\text{tot}} \) is given by Equations (22) to (25), and in terms of the variables \((u, z, \varepsilon)\), \( \sigma \) becomes,

\[
\sigma = \frac{T_{1}}{T_{2}} \left( \frac{V_{u}}{V_{1}} + \frac{1}{V_{1}} \ln z \right) (z - \varepsilon),
\]

(34)

where, thanks to the endoreversibility condition, we have used the thermostatic results \( V_{2} / V_{1} = V_{3} / V_{4} \) and \( V_{2} = V_{3} (T_{3N} / T_{4N})^{\lambda} \), where \( \lambda \) is given by Equation (29).

With Equations (26) and (34) the expression for the ecological function becomes

\[
E = aT_{1} \left( \frac{1 + \varepsilon - 2z}{1} \right) \frac{(1 + \lambda \ln z)}{1 + \varepsilon - 2z - \varepsilon z}.
\]

(35)

Figure 3 shows the behavior of \( P / aT_{1}, \sigma / aT_{1} \) and \( E / aT_{1} \) in the \( u \) constant plane, at \( \lambda = 0 \) and \( \varepsilon \) a given constant value. It is apparent that the maximum power output is achieved with high production of entropy, it is also apparent that zero entropy production is achieved with zero power output, while the function \( E \) represents the maximum possible power output with the minimum possible entropy production.

Upon maximizing the two variables function \( E = E(u, z) \) \((\varepsilon \) defined positive and \( \lambda \) defined semipositive, being external parameters), we obtain for \( \partial E / \partial u = 0 \) and \( \partial E / \partial z = 0 \), at first \( u = u(z) \), as in case of maximizing power output, and later the following relation between the variables \( z \) and \( u_{c} \)

\[
[2(1 + \lambda \ln z)z - \lambda(1 + \varepsilon - 2z)](z - \varepsilon)(z - \varepsilon) = (1 + \varepsilon - 2z)(1 + \lambda \ln z)(1 - u)\varepsilon z.
\]

(36)
Substituting $u$ from (27) in Equation (36) it is obtain the equation that $z$ obeys at the maximum of the ecological function, namely,

$$
[2(1 + \lambda \ln z)z - \lambda(1 + \varepsilon - 2z)](z - \varepsilon) = (1 + \varepsilon - 2z)(1 + \lambda \ln z)\varepsilon.
$$

If we suppose $z = z(\lambda)$ given by the power expansion,

$$
z_p = b_0 + b_1 \lambda + b_2 \lambda^2 + b_3 \lambda^3 + \ldots,
$$

we find, upon taking the implicit successive derivatives of $z_p$ with respect to $\lambda$ in Equation (37) and equating them with the coefficients $b_i$ in Equation (38),

$$
z_E = \frac{1}{2} \varepsilon + \varepsilon^2 \left[ 1 + \frac{1}{4} (1 + 3\varepsilon) \sqrt{\frac{2}{\varepsilon + \varepsilon^2}} - 1 \right] \lambda + \left[ \frac{1}{16} (1 + 3\varepsilon) \frac{1}{\varepsilon + \varepsilon^2} - \frac{2}{2 \sqrt{\varepsilon + \varepsilon^2}} \ln \sqrt{\frac{1}{2} (\varepsilon + \varepsilon^2)} \right] \lambda^2 + O(\lambda^3)
$$

Furthermore, using (39), we can write the efficiency as a power series in $\lambda$,

$$
\eta_E = 1 - z_E(\varepsilon, \lambda)
$$

In the particular case when $\lambda = 0$ we find the value

$$
z_{EO}(\varepsilon, \lambda = 0) = \sqrt{\frac{\varepsilon + \varepsilon^2}{2}},
$$

and the corresponding value for the ecological efficiency with instantaneous adiabats is as:

$$
\eta_{EO} = 1 - z_{EO}(\varepsilon, \lambda = 0) = 1 - \sqrt{\frac{1}{2} (\varepsilon + \varepsilon^2)},
$$
which is the maximum possible one, since all the terms in Eq.(39) are positive.

2.3 The linear approximation

As we can see in Equations (31) and (39), it can be taken a linear approximation for the efficiency \( \eta \) in terms of compression ratio, namely \( V_{\text{max}} / V_{\text{min}} \), and of the ratio \( T_C / T_H \), obtaining an expression like \( F(\eta, V_{\text{max}} / V_{\text{min}}, T_C / T_H) = 0 \), with the same form regardless it was obtained by maximization of power output or maximization of ecological function. It permits analyze the behavior of compression ratio in respect to \( T_C / T_H \). It can verified that \( r_c \to \infty \) and \( \lambda \to 0 \) lead to the Curzon-Ahlborn-Novikov efficiency, now written as \( \eta_{\text{CAN}} = \eta_p(\lambda = 0) = \eta_{\text{PO}} \). From (31) the linear approximation can be obtained,

\[
\eta_{\text{PL}}(\lambda) = 1 - \sqrt{e} - \frac{1}{2}(1 - \sqrt{e})^2 \lambda, \tag{43}
\]

and the corresponding linear approximation of ecological efficiency is as,

\[
\eta_{\text{EL}}(\lambda) = 1 - \sqrt{2(e^2 + e)} - \left[ \frac{1}{4}(1 + 3e) - \sqrt{\frac{1}{2}(e^2 + e)} \right] \lambda. \tag{44}
\]

As can be seen, the linear approximation of efficiency, maximizing power output or ecological function, has the form,

\[
\eta_{\text{IL}}(e, \lambda) = \eta_{\text{PO}} - b_j(e) \lambda = \eta_{\text{PO}} - \frac{b_j(e)}{(\gamma - 1) \ln r_c}, \tag{45}
\]

where \( b_j \) is de coefficient of linear term in \( \lambda \), being \( \lambda = [(\gamma - 1) \ln r_c]^{-1} \), and the subscript \( J \) is substituting by \( P \) or \( E \), for each of cases: maximization of power output or maximization of ecological function. That is, for maximum power output we have \( \eta_{\text{PL}} \), \( \eta_p \) and \( b_p \); and for maximum ecological function we have \( \eta_{\text{EL}} \), \( \eta_e \) and \( b_e \). So, for a particular value of efficiency we have \( r_c = r_c(e) \). The general expression of \( r_c(e) \), from (45), is obtain as,

\[
r_c = \exp \left( \frac{b_j}{(\gamma - 1)(\eta_{\text{PO}} - \eta_{\text{IL}})} \right). \tag{46}
\]

Taking \( \eta_{\text{PO}} \) as Curzon and Ahlborn-Novikov efficiency or ecological efficiency, it is true,

\[
0 < \eta_{\text{IL}} < \eta_{\text{PO}}. \tag{47}
\]

A particular value of efficiency \( \eta_{\text{IL}} \) permits find the interval \( 0 < \varepsilon < 1 \) in which \( r_c \) satisfies,

\[
r_c > 1, \tag{48}
\]

and Equation (48) permits find, from (46),

\[
\frac{b_j}{(\gamma - 1)(\eta_{\text{PO}} - \eta_{\text{IL}})} > 0, \tag{49}
\]

which leads to inequality

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as a necessary condition because $\eta_{\infty}$ must be an upper bound for $\eta_{L}$. For monoatomic gases $\gamma = 1.67$, with $\eta_{L}$ as a variable parameter, the variation of $r_C$ can be obtained, and we can see that $r_C \to \infty$ when $\eta_{L} \to \eta_{\infty}$, as it should be. For each temperatures in Table 1 the variation of $r_C$ is obtained from (46). By example in the West Turrock plant, $T_H = 838$ K and $T_C = 298$ K, with $\eta_{PO} = \eta_{CA} = 0.403367$. Figure 4 shows the behavior of $r_C$ respect to $\eta_{PL}$. Using the ecological function for the same plant, $\eta_{EO} = 0.50905$, and Figure 5 shows the behavior of $r_C$ respect to $\eta_{EL}$. There is a minimum value of compression ratio greater than 1. On other hand for a particular value of $r_C$ and for values of the used parameters in Figures 4 and 5, the behavior of $\eta_{L}$ can be considered as function of $\varepsilon = T_C/T_H$, where we can be see the correctness of (50), so $\eta_{L} \to \eta_{\infty}$ only when $\varepsilon \to 1$, as it is shown in Figure 6, for the ecological function with $r_C = 10$, closer to compression values found in thermodynamics textbooks (among others Burghardt, 1982). In addition, the values of efficiency obtained naturally with the linear approximation are closer to real values than the corresponding values of $\eta_{CA}$, and $\eta_{E}$. The physically possible values of $r_C$ take places when the values of $\lambda$ that comply $0 < \lambda < 1$.

Fig. 4. Behavior of $r_C$ in respect to variation of $\eta_{PL}$ in the interval $[0,0.403367]$. 

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In real compressors, named alternative compressors with dead space, percent of volume in the total displacement of a piston into a cylinder is named dead space ratio, defined as 
\[ c = \frac{\text{(volume of dead space)}}{\text{(volume of displacement)}} \] (Burghardt, 1982). In case of a Curzon and Ahlborn cycle \( c = \frac{\text{(minimum volume)}}{\text{(maximum volume)}} \) is the reciprocal of \( r_c \).

Experimentally it is found that \( 3\% \leq c \leq 10\% \), so \( \frac{100}{3} \geq r_c \geq \frac{100}{10} \), or \( 33 \geq r_c \geq 10 \). Compression ratio is a useful parameter to model the behavior of a thermal engines, but it is not easy to include this parameter in design of power plants, would be interesting find a model in which \( r_c \) could be explicitly incorporated in design power plants.

Fig. 5. Behavior of \( r_c \) in respect to variation of \( \eta_{EL} \) in the interval \( [0,0.50905) \).

Fig. 6. Comparison between ecological efficiency at zero order and at linear order.
Supposing these plants are working as a Curzon and Ahlborn cycle, we found that linear approximation of efficiency, Equation (45), permits us to find intervals of efficiency values near to experimental values of efficiency than others. Table 2 shows a comparison between real values and linear approximation values, assuming ideal gas as working fluid \( (\gamma = 1.67) \), making clear the need for a closer approximation, nevertheless table shows the closeness of the linear approximation.

<table>
<thead>
<tr>
<th>Nuclear power plant</th>
<th>( T_C ) (K)</th>
<th>( T_H ) (K)</th>
<th>( \eta_{obs} )</th>
<th>( \eta_{EL} ) for ( 10 \leq r_C &lt; 33 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Doel 4 (Belgium)</td>
<td>283</td>
<td>566</td>
<td>0.35000</td>
<td>0.37944 to 0.38224</td>
</tr>
<tr>
<td>Almaraz II (Spain)</td>
<td>290</td>
<td>600</td>
<td>0.34500</td>
<td>0.39234 to 0.39539</td>
</tr>
<tr>
<td>Sizewell B, (UK)</td>
<td>288</td>
<td>581</td>
<td>0.36300</td>
<td>0.38277 to 0.38563</td>
</tr>
<tr>
<td>Cofrentes (Spain)</td>
<td>289</td>
<td>562</td>
<td>0.34000</td>
<td>0.36844 to 0.37103</td>
</tr>
<tr>
<td>Heysham (UK)</td>
<td>288</td>
<td>727</td>
<td>0.40000</td>
<td>0.46036 to 0.46506</td>
</tr>
</tbody>
</table>

Table 2. Comparison of values of experimental efficiencies and values of linear ecological approximation.

3. Non-instantaneous adiabats with Dulong-Petit’s heat transfer law

The ecological efficiency has also been calculated using Dulong and Petit’s heat transfer law (Angulo-Brown & Páez-Hernández, 1993; Arias-Hernández & Angulo-Brown, 1994), maximizing ecological function. Their numerical results have shown that the efficiency value changes with the heat transfer law one assumes. Velasco et al. (2000) studied both the power and the ecological function optimizations, using Newton’s heat transfer law. It is worthwhile to point out that in all of the above quoted calculations the time for the adiabatic processes is not taken into account explicitly.

In the present section the power output \( P \), and ecological function \( E \) are chosen to be maximized. Use is made of the more general Dulong and Petit heat transfer law, and the time for all the processes of the Curzon and Ahlborn cycle is explicitly taken into account, to see if the construction of a function \( \eta_{PDP} = \eta_{PDP}(\lambda, \epsilon) \) and \( \eta_{EDP} = \eta_{EDP}(\lambda, \epsilon) \) is possible. That the time for the adiabats can in principle to be an arbitrarily chosen function of the time of the isothems, here however it is chosen in the same way as in previous section for the purposes of comparison. The Dulong and Petit law has been chosen because the main occurring heat transfers are conduction through the wall separating the working fluid from the thermal bath, and convection takes place within the working fluid. Radiative heat transfer is of smaller magnitude (O’Sullivan, 1990). With the optimization of the power...
output of a Curzon and Ahlborn engine, it is shown an approximate expression for efficiency by means of also the Dulong and Petit’s heat transfer law, and the corresponding zero order term in a power series of the parameter $\lambda$ above cited. We follow the procedure employed in the previous section.

3.1 The power output efficiency

Let us assume a gas in a cylinder with a piston as a working fluid that exchanges heat with the reservoirs like in previous section, and let us use a heat transfer law of the form:

$$\frac{dQ}{dt} = \alpha(T_f - T_i)^k$$  \hspace{1cm} (51)

where $k > 1$, $\alpha$ is the thermal conductance which is assumed the same for both reservoirs, $dQ/dt$ is the rate of heat exchange and $T_i$ and $T_f$ are the temperatures for the heat exchange process considered. From the first law of thermodynamics applied to gas under mechanical equilibrium condition, i.e., $p = p_{ext}$, we obtain

$$\frac{dU}{dt} = \frac{dQ}{dt} - p \frac{dV}{dt}$$  \hspace{1cm} (52)

and assuming an ideal gas as working substance $U = U(T)$. One has in case of isothermal processes $dU/dV = dW/dV = 0$. Using Eq. (51) we obtain, for the isothermal processes that

$$\frac{dQ}{dt} = p \frac{dV}{dt} \quad \text{or} \quad \alpha(T_f - T_i)^k = \frac{RT_i}{V} \frac{dV}{dt}.$$  \hspace{1cm} (53)

Equation (53) implies that the time of the process along the first isothermal process is

$$t_1 = \frac{RT_{1WV}}{\alpha(T_f - T_{1WV})^k} \ln \frac{V_2}{V_1}$$  \hspace{1cm} (54)

and analogously, the time along the second isothermal process is

$$t_3 = \frac{RT_{3VW}}{\alpha(T_f - T_{3VW})^k} \ln \frac{V_3}{V_4}.$$  \hspace{1cm} (55)

The corresponding heat exchanged $Q_{H}$ and $Q_{C}$ become, respectively,

$$Q_H = RT_{1WV} \ln \frac{V_2}{V_1}, \quad Q_C = RT_{3VW} \ln \frac{V_4}{V_3},$$  \hspace{1cm} (56)

where, $R$ is the general gas constant and $V_1, V_2, V_3, V_4$, are the corresponding volumes for the states 1,2,3,4 in Figure 1.

While it is true that the speed for the adiabatic branches is independent from the speed of the isothermal ones in the cycle, but with a non null value, in order to obtain a more realistic result it will be assumed that their speed follows a similar law to the isothermal ones. The previous assumption means that the rate of change of volume in the first adiabat is the same that in the first isotherm. Under this assumption, the time along the adiabatic processes is respectively,
where $\gamma = \frac{C_p}{C_v}$ has been used. With these results we can now compute the form for the power output, given by

$$ p = \frac{W}{t_{tot}} = \frac{Q_1 + Q_2}{t_{tot}}, $$

(58)

where $t_{tot} = t_1 + t_2 + t_3 + t_4$. Power output is written as

$$ t_{TOT} = \frac{R}{\alpha} \left[ \frac{T_{HV}}{(T_H - T_{HV})^k} + \frac{T_{CW}}{(T_C - T_{CW})^k} \right] \ln \frac{\gamma z}{\gamma}, $$

(59)

by using $V_2 / V_1 = V_3 / V_4$ and $V_2 = V_3 (T_{CW} / T_{HV})^{\alpha_k}$; so that after making the exchange of variables as in Equation (26), $P$ becomes,

$$ P = T_{I}^{\alpha}(1-z)(1+\alpha \ln z), $$

(60)

with the same parameters as in previous section. By means of $\partial P / \partial u = 0$ and $\partial P / \partial z = 0$ we obtain,

$$ u = \frac{z^{\frac{2}{k}} + \epsilon}{z + z^{\frac{2}{k}}}, $$

(61)

and,

$$ [-(1 + \lambda \ln z)(zu - \epsilon) + (1-z)(zu - \epsilon) + zku(1-z)(1 + \lambda \ln z)] \left( (zu - \epsilon)^k + z(1 - u)^k \right) $$

$$ -z(1-z)(1+\lambda \ln z)(zu - \epsilon) \left( uk(zu - \epsilon)^{k-1} + (1 - u)^k \right) = 0 $$

(62)

Substituting the variable $u$ in Equation (62) with the help of Eq. (61), the resulting expression is the following one, which shows the implicit function $z = z(\lambda, \epsilon)$, for a given $k$,

$$ \left[ z^{\frac{2}{k}} (z - \epsilon) \left( \lambda(1-z) - z(1+\lambda \ln z) + z\epsilon(z + \epsilon)(1-z)(1 + \lambda \ln z) \right) (z^{\frac{2}{k}} + z) \right] z^{\frac{2}{k}} + z) $$

$$ -z(1-z)(1+\lambda \ln z) \left[ z^2 + \epsilon z^{\frac{2}{k}} + z^{\frac{2}{k}} (z - \epsilon) \right] = 0. $$

(63)

Because the solution of Eq. (63) is not analytically feasible when $k$ is not an integer, the case discussed here is $k = 5/4$, the Dulong and Petit’s heat transfer law. So one can take the reasonable approximations only for the exponents in Equation (63),

$$ \frac{2}{k+1} \approx 1 \quad \text{and} \quad \frac{2k}{k+1} \approx 1 $$

(64)
obtaining

\[(1 + \lambda)((k\varepsilon + zk)(1 - z) - z(\varepsilon - z)) + \lambda(1 - z)(1 - \varepsilon) - (1 + \lambda \ln z)(1 - z)z = 0.\] (65)

Equation (65) allows to obtain the explicit expression for the function \(z = z(\varepsilon, k)\) for \(\lambda = 0\),

\[z_{OP}(\varepsilon, k) = \frac{(1 - k)(1 - \varepsilon) \pm \sqrt{(\varepsilon - 1)^2(1 - k)^2 + 4k^2\varepsilon}}{2k}.\] (66)

Taking now \(k = 5/4\) in Equation (66) we obtain the following value for the physically acceptable solution of (63), namely,

\[z_{OPDP} = \frac{1 - \varepsilon + \sqrt{\varepsilon^2 + 9\varepsilon + 1}}{10}.\] (67)

The numerical results for \(\eta_{OPDP} = 1 - z_{OPDP}\) are shown in Table 3, compared with \(\eta_{CAN}\) and the observed efficiency \(\eta_{obs}\), where can be seen that are in good agreement with the reported values. Figure 7 shows the comparison between \(\eta_{OPDP}\) and \(\eta_{CAN}\) with the temperatures of the reservoirs in real plants (Angulo-Brown & Páez-Hernández, 1993; Velasco et al., 2000).

Fig. 7. Comparison between \(\eta_{OPDP}\) obtained here and \(\eta_{CAN}\), in real plants.
Now assuming that $z$ obtained from equation (65) can be expressed as a power series in the parameter $\lambda$, we have the following expression for $\eta_{PDP}$:

$$\eta_{PDP} = 1 - z_{PDP}(\lambda, \varepsilon) = 1 - z_{OPDP}[1 + B_1(\varepsilon)\lambda + B_2(\varepsilon)\lambda^2 + O(\lambda^3)].$$  (68)

We can find the coefficients $B_j$, $j = 1, 2, \ldots$, etc., through successive derivatives respect to $\lambda$.

The two first ones coefficients are:

$$B_1(\varepsilon) = \frac{16(1 - z_{OPDP})(\varepsilon - z_{OPDP})}{z_{OPDP}(5 - 4\varepsilon - 40z_{OPDP})}$$  (69)

and

$$B_2 = \frac{4(z_{OPDP} - 1)(z_{OPDP} - \varepsilon)}{(1 + 9\varepsilon - 10z_{OPDP})^2} \left\{ \frac{[(1 - \varepsilon + 10z_{OPDP})\ln z_{OPDP} + 8z_{OPDP} - 4\varepsilon - 4](\varepsilon + 1 - 10z_{OPDP})}{1 + 9\varepsilon - 10z_{OPDP}} \right\} \times$$

$$\frac{40(z_{OPDP} - 1)(z_{OPDP} - \varepsilon)}{1 + 9\varepsilon - 10z_{OPDP}} - \left\{ (9\varepsilon - 1 - 10z_{OPDP})\ln z_{OPDP} + 4 + 4\varepsilon - 8z_{OPDP} \right\}$$  (70)

which are positive for $\varepsilon$ values in the interval $0 < \varepsilon < 1$, as we can see in Figure 8.

Fig. 8. First and second order coefficients, $B_1 = B_1(\varepsilon)$, $B_2 = B_2(\varepsilon)$, of (2.21) for $0 < \varepsilon < 1$. 

Table 3. Comparison of Curzon and Ahlborn and observed efficiencies with the here approximated obtained efficiency.

<table>
<thead>
<tr>
<th>Power plant</th>
<th>$T_C$</th>
<th>$T_H$</th>
<th>$\eta_{CAN}$</th>
<th>$\eta_{OPDP}$</th>
<th>$\eta_{OBS}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam power plant, West Thurrock, U K</td>
<td>298</td>
<td>838</td>
<td>0.40367</td>
<td>0.33577</td>
<td>0.360</td>
</tr>
<tr>
<td>Geothermal steam plant, Lardarello, Italy</td>
<td>353</td>
<td>523</td>
<td>0.17845</td>
<td>0.1453</td>
<td>0.160</td>
</tr>
<tr>
<td>Steam power plant, U S A</td>
<td>298</td>
<td>923</td>
<td>0.43179</td>
<td>0.36006</td>
<td>0.400</td>
</tr>
<tr>
<td>Combined cycle plant (steam-mercury), U S A</td>
<td>298</td>
<td>783</td>
<td>0.38308</td>
<td>0.31804</td>
<td>0.340</td>
</tr>
</tbody>
</table>
3.2 Ecological efficiency

Now we consider the entropy production given by

$$\sigma = \frac{\Delta S}{t_{tot}} = \frac{1}{t_{tot}} \left( \frac{Q_H}{T_H} + \frac{Q_c}{T_c} \right)$$  \(\text{(71)}\)

which becomes,

$$\sigma = \frac{\alpha T_H^\lambda (1 + \lambda \ln z)(z - \varepsilon)}{T_c \left( \frac{1}{(1-u)} + \frac{\varepsilon}{(zu-z^2)} \right)}$$  \(\text{(72)}\)

so that the ecological function for Curzon and Ahlborn engine takes the form,

$$E(x,z) = \frac{T_H^\lambda \alpha (1 + \lambda \ln z)(1 + \varepsilon - 2z)}{(1-u)^{\varepsilon} + \frac{\varepsilon}{(zu-z^2)}}$$  \(\text{(73)}\)

As in the previous sections we find the function \(z(\varepsilon)\) that follows from the maximization of function \(E(u,z)\), which permits obtain the corresponding efficiency for the value \(k = 5/4\), namely, the Dulong and Petit heat transfer law, previously defined. Upon setting \(\partial E / \partial u = 0\) and \(\partial E / \partial z = 0\), we obtain from the first condition that

$$u = \frac{Z^{\frac{3}{2}} + \varepsilon}{Z + Z^{\frac{3}{2}}}$$  \(\text{(74)}\)

and from the second one,

$$\frac{(1 + \varepsilon - 2z)(z - \varepsilon)}{(1 + \lambda \ln z)(1 + \varepsilon - 2z)(zu - \varepsilon - kuz)z} - \frac{(1-u)^\varepsilon}{(zu - \varepsilon)^{\varepsilon} + z(1-u)^{\varepsilon}} = 0.$$  \(\text{(75)}\)

Substituting now Equation (74) for \(u\) in Equation (75) we are led to the following expression,

$$(-2(1 + \lambda \ln z)z + (1 + \varepsilon - 2z)\lambda)z^2 + (zu-z^2)z^2 - (zu-z)^2 = (1 + \lambda \ln z)(1 + \varepsilon - 2z)z^2 - (zu-z)^2.$$  \(\text{(76)}\)

The analytical solution of Eq. (76) is not feasible when the exponents of \(z\) are not integers, which is the present case, because with \(k = 5/4\), Dulong and Petit’s heat transfer law, one has \((k+3)/(k+1) = 17/9\) and \(2/(k+1) = 8/9\).

The numerical solution of Eq. (76) shows that any solution falls into the region bounded by solutions for \(\lambda = 0\) and \(\lambda = 1\), (Ladino-Luna, 2008). It can be appreciated that within the interval \(0 \leq \varepsilon \leq 1\), which is the only one physically relevant, the curve (76) can be fitted with a parabolic curve. The simplest approximation that allows for a parabolic fit for \(0 \leq \lambda \leq 1\) is the following modification of the exponents:

$$\frac{k+3}{k+1} \approx 2, \quad \frac{2}{k+1} \approx 1.$$  \(\text{(77)}\)
These approximations allow the following approximate analytical expression for $z(\varepsilon, \lambda)$

$$2(-2(1 + \lambda \ln z)z + (1 + \varepsilon - 2z)\lambda)(z - \varepsilon) - (1 + \lambda \ln z)(1 + \varepsilon - 2z)((z - \varepsilon) - (z + \varepsilon)k) = 0. \quad (78)$$

For the case $\lambda = 0$, that corresponds to instantaneous adiabats, and taking $k = 5/4$ in Equation (78), the value of the positive root $z_{OEDP}(\varepsilon)$ is obtained,

$$z_{OEDP} = \frac{1 - \varepsilon + \sqrt{649\varepsilon^2 + 646\varepsilon + 1}}{36}. \quad (79)$$

The negative root has no physical meaning because efficiencies must always be positive.

Figure 9 shows a comparison between fitted numerical values of $\eta_{MEDP}$ (Angulo-Brown & Páez-Hernández, 1993; Árias-Hernández & Angulo-brown, 1994) and $\eta_{OEDP} = 1 - z_{OEDP}$.

![Fig. 9. Approximated Ecological efficiency $\eta_{OEDP}$, compared with a fitted of $\eta_{MEDP}$.](image1)

![Fig. 10. Ecological efficiency for Newton's heat transfer and Dulong-Petit's heat transfer.](image2)
Notice that \( \eta_{OEDP} \) is a better result from a theoretical point of view, because it goes to zero as \( \varepsilon \to 1 \) as it should be. Figure 10 shows the comparison between \( \eta_e \) and \( \eta_{OEDP} \) where \( \eta_{OEDP} < \eta_e \).

Let it be assumed now that \( z \) given by equation (78) is a power series in the parameter \( \lambda \), i.e.,

\[
\eta_{EDP} = 1 - z_{EDP}(\lambda, \varepsilon) = 1 - z_{EDP}(1 + b_1(\varepsilon)\lambda + b_2(\varepsilon)\lambda^2 + O(\lambda^3)),
\]

and let us proceed to the calculation of the coefficients of the powers in \( \lambda \). To this end one takes \( z_0 = z_{EDP}(\varepsilon, \lambda = 0) \) and from (78) the coefficients are calculated by successively taking the derivative with respect to \( \lambda \) and evaluating at \( \lambda = 0 \). The first two are:

\[
b_1(\varepsilon) = \frac{-2z_0 + 2\varepsilon - 6z_0\varepsilon + 2\varepsilon^2 + 4z_0^2}{z_0(-9z_0 - \frac{4}{3}\varepsilon + \frac{1}{4})}, \tag{81}
\]

and

\[
b_2(\varepsilon) = \frac{1}{2z_0}(A_1(\varepsilon) + A_2(\varepsilon)), \tag{82}
\]

where

\[
A_1(\varepsilon) = \frac{4b_1}{(1 - \varepsilon - 2z_0)^2} \left\{ -160(z_0 - \varepsilon)(1 + \varepsilon - 2z_0) + \left[ (-36z_0 + 9\varepsilon + 1) \ln z_0 - 18z_0 + 9\varepsilon + 1 + \frac{9(\varepsilon + \varepsilon^2)}{z_0} + 8(1 + \varepsilon - 2z_0) - 16(z_0 - \varepsilon) \right] \left[ -1 + \eta + 20z_0 \right] \right\}, \tag{83}
\]

and

\[
A_2(\varepsilon) = \frac{-8(z_0 - \varepsilon)(1 + \varepsilon - 2z_0)}{(1 - \varepsilon - 2z_0)^2} \left[ (36z_0 + \varepsilon - 1) \ln z_0 + 48z_0 - 40\varepsilon - 8 + \frac{1 + \varepsilon - 2z_0}{z_0}(z_0 + 9\varepsilon) \right] \tag{84}
\]

Fig. 11. First and second order coefficients \( b_1 = b_1(\varepsilon) \) and \( b_2 = b_2(\varepsilon) \) in (80)
Non-Instantaneous Adiabats in Finite Time

To assume that (80) is valid it requires that \( \eta \leq 1 \). For this to be so, \( b_1 \) and \( b_2 \) must be positive when \( 0 < \varepsilon < 1 \) and when \( \lambda < 1 \), i.e. there must exist an interval for \( \varepsilon \) into which the coefficients have positive values, near to zero. Figure 11 shows that in fact this is correct. This guarantees that Eq. (80) is valid and that \( 1 - z_0 \) is an upper bound of \( \eta \), but not the upper bound \( \eta_C \).

4. The van der Waals gas

The internal energy in the case of a van der Waals gas for \( n \) moles, with a change of temperature \( \Delta T = T - T_0 \), at volume \( V \), and with the characteristic constant \( a \) of the system, and the constant heat capacity \( C \) can be written as,

\[
U = nC(T - T_0) - \frac{an^2}{V}. \tag{85}
\]

So that taking the temporary derivative for an adiabatic process,

\[
\frac{dU}{dt} = \frac{an^2}{V^2} \frac{dV}{dt}, \tag{86}
\]

the first law of thermodynamics leads to

\[
\frac{dU}{dt} = \frac{dQ}{dt} - \frac{p_{ext}}{dt} \frac{dV}{dt} - (p - p_{ext}) \frac{dV}{dt}, \tag{87}
\]

taking \( p \) as the internal pressure and \( p_{ext} \) as the pressure of surroundings. Combining Equations (86) and Eq. (87), in mechanical equilibrium, we obtain

\[
\frac{an^2}{V^2} \frac{dV}{dt} = \frac{dQ}{dt} - p \frac{dV}{dt}, \tag{88}
\]

so that, for a non linear heat transfer law, more general than Dulong and Petit heat transfer law, as

\[
\frac{dQ}{dt} = \alpha(T - T_0)^{k}, \tag{89}
\]

with the constant thermal conductance \( \alpha \), and the constant exponent \( k \), \( k > 1 \), from Equation. (88), in an isothermal process,

\[
\frac{an^2}{V^2} + p \frac{dV}{dt} = \alpha(T - T_0)^{k}. \tag{90}
\]

On other hand, the state equation for a van der Waals gas, with a constant \( b \) characteristic of the system, which is a more realistic model for a real gas, takes the following expression, with constant parameters \( a \) and \( b \),

\[
p = \frac{nRT}{V - nb} \frac{an^2}{V^2}, \tag{91}
\]
whose derivative respect $T$ at $p = \text{constant}$ leads to

$$0 = \frac{nR}{V - nb} + nRT \left( \frac{1}{(V - nb)^2} \frac{\partial V}{\partial T} + \frac{2a}{V^2} \frac{\partial V}{\partial T} \right). \quad (92)$$

By taking $n = 1$, Equation (91) into Equation (90) leads to

$$\frac{RT_0}{V - b} \frac{dV}{dt} = \alpha(T - T_0)^k. \quad (93)$$

In the case of a Curzon and Ahlborn cycle (Figure 1), for the heat exchange between the engine and the reservoirs, Equation (93) leads to the time of the isothermal processes by taking its integration. Moreover in the case of adiabatic processes $dQ/dt = 0$, so that Equation (87) reduces to

$$\frac{dU}{dt} = -p \frac{dV}{dt}, \quad (94)$$

and one can obtain

$$C_V \ln T = -R \ln(V - b), \quad (95)$$

or as it is usually written,

$$T(V - b)^{\frac{R}{C_V}} = \text{constant}. \quad (96)$$

Also, the duration time of the adiabatic processes can be obtained by integration of (93). Therefore the duration time of all processes in the cycle can be obtained from Equation (94), and Equation (96) leads to the relation between temperatures of the engine and the changes of volume in the adiabatic transformation.

### 4.1 Power output and ecological function

Taking into account the difference of temperatures between the engine and its reservoirs (Figure 1), it can be written the time for all of the processes in the cycle from Equation (93)

For the isothermal processes, Eq. (93) can be written as

$$\frac{RT_{HV}}{V - b} \frac{dV}{dt} = \alpha(T_{HI} - T_{HV})^k, \quad \text{and} \quad \frac{RT_{CW}}{V - b} \frac{dV}{dt} = \alpha(T_{CIW} - T_{CW})^k, \quad (97)$$

and by direct integration of Equations (97) we obtain

$$t_1 = \frac{RT_{HV}}{\alpha(T_{HI} - T_{HV})^k} \ln \frac{V_2 - b}{V_1 - b}, \quad \text{and} \quad t_2 = \frac{RT_{CW}}{\alpha(T_{CIW} - T_{CW})^k} \ln \frac{V_4 - b}{V_3 - b}, \quad (98)$$

Analogously, the time for the adiabatic processes can be obtained as

$$t_3 = \frac{RT_{HV}}{\alpha(T_{HI} - T_{HV})^k} \ln \frac{V_2 - b}{V_1 - b}, \quad \text{and} \quad t_4 = \frac{RT_{CW}}{\alpha(T_{CIW} - T_{CW})^k} \ln \frac{V_4 - b}{V_3 - b}, \quad (99)$$

Now, taking into account Equation (96), for the first adiabatic process,
T_{HV}(V_2-b)^{\frac{1}{\gamma}} = T_{CV}(V_3-b)^{\frac{1}{\gamma}}, \text{ or, } \ln \frac{V_3-b}{V_2-b} = \frac{C_v}{R} \ln \frac{T_{rev}}{T_{cv}}, \quad (100)

and for the second adiabatic process,

T_{CV}(V_4-b)^{\frac{1}{\gamma}} = T_{HV}(V_1-b)^{\frac{1}{\gamma}}, \text{ or, } \ln \frac{V_4-b}{V_1-b} = \frac{C_v}{R} \ln \frac{T_{rev}}{T_{cv}}, \quad (101)

and the combination of Eqs. (100) and (101) allows to obtain the relation

\frac{V_3-b}{V_2-b} = \frac{V_4-b}{V_1-b}, \quad (102)

The power output \( P \) can be written simplyfing with the same used parameters as,

\[ P = \alpha T_H^k (1-z) \left[ \alpha_{HV} \ln \frac{z}{1-z} + \frac{z}{(1-z)^2} \right], \quad (103) \]

where \( \alpha_{HV} = \left( y-1 \right) \ln \frac{V_2-b}{V_1-b} \) \(^{-1} \). One can see that \( b \rightarrow 0 \) leads to \( \alpha_{HV} \rightarrow \alpha \) in Equation (29), and one can see that \( b \rightarrow 0 \) and \( k \rightarrow 1 \) reduce (103) to expression of \( P \), such as it was found previously (Ladino-Luna, 2002, 2005). An expression of power series in \( \alpha_{HV} \) leads to the efficiency that can be obtained following the procedure in those references.

In the case of ecological function it is necessary to build the entropy production \( \sigma \), \( \sigma = \frac{\Delta S}{\alpha_{HV}} \), so that (33) can be written since

\[ \Delta S = \Delta S_{1 \rightarrow 2} + \Delta S_{3 \rightarrow 4}, \quad (104) \]

where \( \Delta S_{1 \rightarrow 2} \) is the change of entropy in the first isothermal branch and \( \Delta S_{3 \rightarrow 4} \) is the change of entropy at the second isothermal branch. For heat reservoirs, \( \Delta S = \frac{Q}{T} \), assumed as it is only in the transfer processes between the reservoirs and the engine,

\[ \Delta S_{1 \rightarrow 2} = \frac{Q_{1 \rightarrow 2}}{T_H} = R \frac{T_{HV}}{T_H} \ln \frac{V_2-b}{V_1-b}, \quad \text{and} \quad \Delta S_{3 \rightarrow 4} = \frac{Q_{3 \rightarrow 4}}{T_C} = R \frac{T_{CV}}{T_C} \ln \frac{V_4-b}{V_3-b}, \quad (105) \]

so that Eq. (104) can be written as

\[ \Delta S = R \left[ \frac{T_{HV}}{T_H} \ln \frac{V_2-b}{V_1-b} - \frac{T_{CV}}{T_C} \ln \frac{V_4-b}{V_3-b} \right], \quad (106) \]

and by using (102) and (96) one can obtain the entropy production as,

\[ \sigma = \frac{\alpha T_H^k (1-z) \left[ \alpha_{HV} \ln \frac{z}{1-z} + \frac{z}{(1-z)^2} \right]}{1-\alpha_{HV}}, \quad (107) \]

then, by using (3), (98) and (99) the ecological function can be written as

\[ \sigma = \frac{\alpha T_H^k (1-z) \left[ \alpha_{HV} \ln \frac{z}{1-z} + \frac{z}{(1-z)^2} \right]}{1-\alpha_{HV}}, \quad (107) \]

then, by using (3), (98) and (99) the ecological function can be written as
Thermodynamics – Physical Chemistry of Aqueous Systems

\[
E = \frac{\alpha T^4 \left(1 - 2z + \varepsilon\right)}{(1 - 2z) + \varepsilon} \ln \frac{z}{b_2} + O(\varepsilon^3).
\]

One can see that the structure of Eq. (108) leads to the case with Newton’s heat transfer law when the limit \( k \to 1 \) is. It is also obtained the case of Newton heat transfer with an ideal gas as the working substance when \( k = 1 \) and \( b = 0 \). A general form of ecological function and power output function can be obtained by replacing \( \lambda_{VW} \) instead of \( \lambda \), and with approximations for the cases when \( k > 1 \). \( z_{EDP} \) and \( \eta_{EDP} \) (Ladino-Luna, 2008) are modified with the substitution \( V - b \) instead of \( V \).

The corresponding maximization of ecological function taking Dulong-Petit’s heat transfer and a van der Waals gas as the working substance can be found with the substitution \( \lambda_{VW} \) instead of \( \lambda \) in all of the process to build the ecological efficiency. In the case of power output with the same substitution, we obtain the approximate formula for the efficiency when \( \lambda_{VW} \) goes to zero, and a similar power series of the efficiency as a function of \( \lambda_{VW} \),

\[
\eta_{PDPVW} = 1 - z_{PDP}(\lambda_{VW}, \varepsilon) = 1 - z_{OPDP}(1 + b_2(\varepsilon)\lambda_{VW}^2 + b_2(\varepsilon)\lambda_{VW}^2 + O(\lambda_{VW}^3)),
\]

wher \( z_{OPDP} \) is the same approximate efficiency previously found in section 3, following the procedure by Ladino-Luna (2003). At the limit \( \lambda_{VW} \to 0 \) we obtain \( \eta_{PDPVW}(\lambda_{VW} = 0) = \eta_{OPDP} \) where \( \eta_{OPDP} \) is the same approximate efficiency found in Section 3. As one can see, \( \eta_{PDPVW}(\lambda_{VW} = 0) < \eta_{CAN} \), so \( \eta_{CAN} \) can be consider as an upper bound for the efficiencies that taking into account the time of the adiabatic processes in the Curzon and Ahlborn cycle.

5. Conclusions

A first result is the fact that the efficiency for a Carnot type engine depends on the size of the engine, the compression ratio, as represented by the parameter \( \lambda \sim \left[\ln(V_3 / V_1)\right]^{-1} \) or \( \lambda_{VW} = \left[(\nu - 1) \ln V_3 / V_1\right]^{-1} \). Leading term in power series corresponds to the exact value numerically calculated without explicitly taking into account the dependence on \( \lambda \), and is an upper bound for the value of the efficiency \( \eta_{DP} \); in fact the larger the ratio \( V_3 / V_1 \) (or \( V_3 / V_1 / (V_3 - b) / (V_1 - b) \)), the larger the efficiency becomes. The comparison between the upper bound of the efficiency calculated with the proposed approximations and a fitted curve obtained of the numerical values from cited references shows the goodness of the made approximations in case of \( k = 5 / 4 \). It is worthwhile mentioning that exist an interval for \( \varepsilon, \varepsilon \sim 0.5 \), were the approximation employed is acceptable within 5% of the true value of \( z(\varepsilon) \) for \( 0 \leq \varepsilon \leq 1 \) as shown. A last result is shown in Figures where one can appreciate that the difference between using Newton’s or Dulong-Petit’s heat transfer laws does not lead to an important difference in the value of the ecological efficiency. It has also been shown that for the Dulong-Petit heat transfer law and the ideal gas law, the limit \( \lambda \to 0 \) reduces to the reported result. Also, the results suggest that can be extended a new interpretation as the way to real performance of the thermal plants. It shows a mixture between Newton and Dulong-Petit heat transfer laws. Non-endoreversible cycles could be analyzed using non-instantaneous adiabats together with non-linear heat transfer.
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7. References


Thermodynamics is one of the most exciting branches of physical chemistry which has greatly contributed to the modern science. Being concentrated on a wide range of applications of thermodynamics, this book gathers a series of contributions by the finest scientists in the world, gathered in an orderly manner. It can be used in post-graduate courses for students and as a reference book, as it is written in a language pleasing to the reader. It can also serve as a reference material for researchers to whom the thermodynamics is one of the area of interest.

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