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Ecological optimization of endoreversible chemical engines

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Abstract
Optimal ecological performances of endoreversible chemical engine cycles with both linear and diffusive mass transfer laws are derived by taking an ecological optimization criterion as the objective, which consists of maximizing a function representing the best compromise between the power output and entropy production rate of the chemical engines. Numerical examples are given to show the effects of mass-reservoir chemical potential ratio and mass-transfer coefficient ratio on the ecological function versus the efficiency characteristic of the cycles. The results can provide some theoretical guidelines for the design of practical chemical engines.
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Keywords: Finite time thermodynamics; Chemical engine cycle; Ecological optimization; Finite mass transfer rate; Linear mass transfer law; Diffusive mass transfer law.

1. Introduction
In the last three decades, finite-time thermodynamics (FTT) has been developed [1-15]. This approach consists of an extension of classical equilibrium thermodynamics by the inclusion of some classes of irreversibilities in the thermodynamic formalism. Finite-time thermodynamics is a powerful tool for the performance analysis and optimization of real engineering cycles. Most of the previous works have concentrated on power optimization, or the minimization of the fixed cost for a heat engine and the thermal-efficiency optimization. Alternatively, Angulo-Brown *et al.* [16] proposed the ecological criterion $E_1 = P - T_L\sigma$ for finite-time Carnot heat engines, where T_L is the temperature of cold heat reservoir, P is the power output and σ is the entropy generation rate. Yan [17] showed that it might be more reasonable to use $E_2 = P - T_0\sigma$ if the cold-reservoir temperature T_L is not equal to the environment temperature T_0 from the point of view of exergy analysis. The optimization of the ecological criterion represents a compromise between the power output P and the loss power $T_0\sigma$, which is produced by entropy generation in the system and its surroundings. Furthermore, based on the view of point of exergy analysis, Refs. [18-26] provided a unified exergy-based ecological optimization objective for all of thermodynamic cycles, that is $E = A/\tau - T_0\Delta S/\tau = A/\tau - T_0\sigma$, where A is the exergy output of the cycle, T_0 is the environment temperature of the cycle, ΔS is the entropy generation of the cycle, τ is the cycle period, and σ is the entropy generation rate of the cycle. It represents the best compromise between the exergy output rate and the exergy loss rate (entropy generation rate) of the thermodynamic cycles. Many researchers have studied the ecological optimization for various thermodynamic cycles [18-30].

De vos [31] analyzed the performance of isothermal endoreversible chemical engine. Gordon [32] and Gordon and Orlov [33] obtained the maximum work output [32] and the maximum power output [33] of a class of isothermal endoreversible chemical engines with the sole irreversibility of mass transfer. Chen *et al*. [34, 35] derived the optimal relation between the power output and the second law efficiency of the isothermal endoreversible chemical engines with the sole irreversibility of mass transfer [34] and analyzed the effect of mass leakage on the performance of isothermal chemical engines [35]. Chen *et al*. [36, 37] established a new model of a class of combined-cycle isothermal endoreversible chemical engines, derived the optimal relation between the power output and the second law efficiency of the combined-cycle isothermal endoreversible chemical engines with the sole irreversibility of mass transfer [36], and analyzed the effect of mass leakage on the performance of combined-cycle isothermal chemical engines [37]. Lin *et al*. [38] established a model of a generalized irreversible isothermal chemical engine with irreversibility of mass transfer, mass leakage and internal loss, and derived the optimal relation between the power output and the first law efficiency of the irreversible isothermal chemical engine. Tsirlin *et al*. [39] also derived the minimum entropy generation rate and the maximum power output of a class of isothermal endoreversible chemical engines. Recently, Chen *et al.* [40] and Xia *et al.* [41, 42] modeled and optimized the performance of endoreversible chemical engines [40], endoreversible two-mass-reservoir chemical pumps [41] and endoreversible three-mass-reservoir chemical potential transformer [42] with the diffusive mass transfer law. On the basis of Ref. [31-42], the ecological optimization of an endoreversible chemical engine is considered in this paper. The characteristics of the ecological function, power output and efficiency of the cycles with both linear and nonlinear mass transfer laws are derived. The numerical examples are given to show the relations among the ecological function, the power output and the efficiency, as well as the effects of mass-reservoir chemical potential ratio and mass-transfer coefficient ratio on the ecological function versus the efficiency characteristic of the chemical engines.

2. Chemical engine model

The schematic diagram of an isothermal endoreversible chemical engine is shown in Figure 1. The two mass reservoirs associated with the chemical engine have chemical potentials of μ_H and μ_L. The configuration of the chemical engine is analogous to that of heat engine with finite heat transfer rate [16, 43]. The chemical engine receives its mass ΔN_1 at chemical potential μ_1 from the high chemical potential reservoir at μ_H in time t_1, and rejects its mass ΔN_2 at chemical potential μ_2 to the low chemical potential reservoir at μ_L in time t_2. Besides the two mass transfer processes between the cyclic working fluid and the mass reservoirs, there also exist other additional branches of the cycle that connect the two mass transfer processes. The additional branches do not have mass transfer, therefore the times spent on the connecting branches without mass transfer is neglected and the cyclic period τ of the chemical engine equals, approximately, the sum of t_1 and t_2, i.e.

$$\tau = t_1 + t_2 \tag{1}$$

The law of mass conservations gives

$$\Delta N_1 = \Delta N_2 = \Delta N^* \tag{2}$$

The power output P and the first law efficiency η of the chemical engine are

$$P = \frac{W}{\tau} = \frac{\mu_1 \Delta N_1 - \mu_2 \Delta N_2}{\tau} \tag{3}$$

$$\eta = \frac{\mu_1 \Delta N_1 - \mu_2 \Delta N_2}{\mu_H \Delta N_1} \tag{4}$$

The entropy production ΔS of the cycle is

$$\Delta S = \frac{\mu_H \Delta N_1 - \mu_L \Delta N_2 - W}{T} = \frac{\mu_H \Delta N_1 - \mu_L \Delta N_2 - (\mu_1 \Delta N_1 - \mu_2 \Delta N_2)}{T} \tag{5}$$

The entropy production rate σ of the cycle is

$$\sigma = \frac{\Delta S}{\tau} = \frac{\mu_H \Delta N_1 - \mu_L \Delta N_2 - W}{\tau T} = \frac{\mu_H \Delta N_1 - \mu_L \Delta N_2 - (\mu_1 \Delta N_1 - \mu_2 \Delta N_2)}{\tau T} \tag{6}$$

where T is the working temperature of the chemical engine.

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Dividing the both sides of Eq. (5) by $\mu_H \Delta N_1$ yields:

$$\frac{\Delta S}{\mu_H \Delta N_1} = \frac{\eta_r - \eta}{T} \tag{7}$$

where $\eta_r = 1 - \mu_L / \mu_H$ is the efficiency of reversible chemical engine.
From Eq. (7), one can obtain

$$\frac{T\Delta S}{\eta_r - \eta} = \mu_H \Delta N_1 \tag{8}$$

Dividing the both sides of Eq. (8) by W yields:

$$\frac{T\Delta S / W}{\eta_r - \eta} = \frac{1}{\eta} \tag{9}$$

From Eq. (9), one can obtain

$$\eta = \eta_r - \frac{T\Delta S}{T\Delta S + W}\eta_r \tag{10}$$

Eq. (10) represents the relation between the practical efficiency and the reversible efficiency. Item $\frac{T\Delta S}{T\Delta S + W}\eta_r$ can be seen as the efficiency of dissipation of the irreversible cycle.
From Eq. (9), one can obtain

$$\begin{aligned} P &= \frac{\eta_r}{\eta_r - \eta} T\sigma - T\sigma \\ &= \frac{\eta_r}{\eta} P - T\sigma \end{aligned} \tag{11}$$

where item $\frac{\eta_r}{\eta} P$ is the power output of reversible chemical engine cycle, item $T\sigma$ can be seen as the dissipation of power output.
Like for the heat engine [16], one can define a function $E^{'}$ represents the compromise between the power output and the dissipation of power output of the chemical engine which called ecological function, i.e.

$$E^{'} = P - T\sigma \tag{12}$$

However, according to Yan [17], it might be more reasonable to use

$$E = P - T_0\sigma \tag{13}$$

If the working temperature T is not equal to the environment temperature T_0 from the point of view of exergy analysis. The optimization of the ecological criterion represents a compromise between the power output P and the loss power $T_0\sigma$, which is produced by entropy generation in the system and its surroundings.
The ecological performance optimization will carried out based on two mass transfer laws.

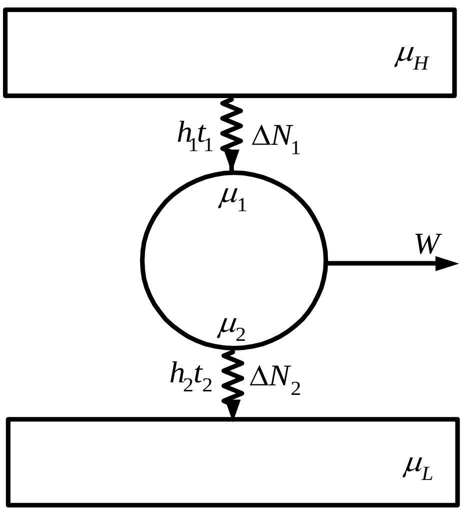

Figure 1. Model of an isothermal endoreversible chemical engine

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3. Linear mass transfer law

It is assumed that the mass exchange obeys the mass transfer law of linear irreversible thermodynamics, i.e.

$$\Delta N_1 = h_1(\mu_H - \mu_1)t_1,\ \Delta N_2 = h_2(\mu_2 - \mu_L)t_2 \tag{14}$$

where h_1 and h_2 are mass-transfer coefficients.

Combining equations (1)-(6), (13) and (14) gives

$$P = \frac{\mu_1 - \mu_2}{[h_1(\mu_H - \mu_1)]^{-1} + [h_2(\mu_2 - \mu_L)]^{-1}} \tag{15}$$

$$\eta = \frac{\mu_1 - \mu_2}{\mu_H} \tag{16}$$

$$\sigma = \frac{1}{T}\frac{\mu_H - \mu_L - (\mu_1 - \mu_2)}{[h_1(\mu_H - \mu_1)]^{-1} + [h_2(\mu_2 - \mu_L)]^{-1}} \tag{17}$$

The ecological function E of the cycle is

$$E = P - T_0\sigma = \frac{(1+\frac{T_0}{T})(\mu_1 - \mu_2) - \frac{T_0}{T}(\mu_H - \mu_L)}{[h_1(\mu_H - \mu_1)]^{-1} + [h_2(\mu_2 - \mu_L)]^{-1}} \tag{18}$$

where T_0 is the environment temperature.

3.1 Fundamental optimal relation

Now, the problem is to determine the optimal ecological function of the chemical engine for a given efficiency. Therefore, one can introduce a Lagrangian function $L = E + \lambda\eta$, where λ is the Lagrangian multiplier, and from the Euler-Lagrange equations $\partial L / \partial\mu_1 = 0$ and $\partial L / \partial\mu_2 = 0$, one can find that the following equation must be satisfied

$$\mu_2 - \mu_L = \sqrt{h_1 / h_2}(\mu_H - \mu_1) \tag{19}$$

Substituting equation (19) into equations (15)-(18) yields the optimal dimensionless ecological function $E^* = E / (h_1\mu_H^2)$, dimensionless power output $P^* = P / (h_1\mu_H^2)$, dimensionless entropy production rate $\sigma^* = \sigma T_0 / (h_1\mu_H^2)$ and the efficiency as follows:

$$E^* = \frac{\{(1+\frac{T_0}{T})[\eta_r - (1+\sqrt{b})x] - \frac{T_0}{T}\eta_r\}x}{1+\sqrt{b}} \tag{20}$$

$$P^* = \frac{[\eta_r - (1+\sqrt{b})x]x}{1+\sqrt{b}} \tag{21}$$

$$\sigma^* = \frac{T_0}{T}x^2 \tag{22}$$

$$\eta = \eta_r - (1+\sqrt{b})x \tag{23}$$

where $x = 1 - \mu_1 / \mu_H$ and $b = h_1 / h_2$. Eliminating $x = 1 - \mu_1 / \mu_H$ from equations (20)-(23) yields the fundamental optimal relations between the dimensionless ecological function, dimensionless power output, dimensionless entropy production rate and the efficiency of the endoreversible chemical engine.

$$E^* = \frac{[(1+\frac{T_0}{T})\eta - \frac{T_0}{T}\eta_r](\eta_r - \eta)}{(1+\sqrt{b})^2} \tag{24}$$

$$P^* = \frac{\eta(\eta_r - \eta)}{(1+\sqrt{b})^2} \tag{25}$$

$$\sigma^* = \frac{T_0}{T}\left(\frac{\eta_r - \eta}{1+\sqrt{b}}\right)^2 \tag{26}$$

3.2 The maximum dimensionless ecological function and corresponding parameters

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Using equation (24) and the extreme condition $\partial E^* / \partial \eta = 0$, one finds that when

$$\eta_{E^*} = \frac{1+2T_0/T}{2(1+T_0/T)}\eta_r \tag{27}$$

The dimensionless ecological function attains its extremum, i.e.

$$E^*_{\max} = \frac{\eta_r^2}{4(1+T_0/T)(1+\sqrt{b})^2} \tag{28}$$

The corresponding dimensionless power output and dimensionless entropy production rate are

$$P^*_{E^*} = \frac{(1+2T_0/T)\eta_r^2}{4(1+T_0/T)^2(1+\sqrt{b})^2} \tag{29}$$

$$\sigma^*_{E^*} = \frac{T_0}{T}\left[\frac{\eta_r}{2(1+T_0/T)(1+\sqrt{b})}\right]^2 \tag{30}$$

3.3 The maximum dimensionless power output and corresponding parameters

Using equation (25) and the extreme condition $dP^* / d\eta = 0$, one finds that when

$$\eta_{P^*} = \frac{1}{2}\eta_r \tag{31}$$

The dimensionless power output attains its extremum, i.e.

$$P^*_{\max} = \frac{\eta_r^2}{4(1+\sqrt{b})^2} \tag{32}$$

The corresponding dimensionless ecological function and dimensionless entropy production rate are

$$E^*_{P^*} = \frac{(1-T_0/T)\eta_r^2}{4(1+\sqrt{b})^2} \tag{33}$$

$$\sigma^*_{P^*} = \frac{T_0}{T}\frac{\eta_r^2}{4(1+\sqrt{b})^2} \tag{34}$$

4. Diffusive mass transfer law

It is assumed that the mass exchange obeys the mass transfer law of nonlinear irreversible thermodynamics, i.e.

$$\Delta N_1 = h_1'(\exp\tfrac{\mu_H}{kT} - \exp\tfrac{\mu_1}{kT})t_1,\ \Delta N_2 = h_2'(\exp\tfrac{\mu_2}{kT} - \exp\tfrac{\mu_L}{kT})t_2 \tag{35}$$

where h_1' and h_2' are mass-transfer coefficients, k is the Boltzmann's constant.

Combining equations (1)-(6), (13) and (35) gives

$$P' = \frac{\mu_1 - \mu_2}{[h_1'(\exp\frac{\mu_H}{kT} - \exp\frac{\mu_1}{kT})]^{-1} + [h_2'(\exp\frac{\mu_2}{kT} - \exp\frac{\mu_L}{kT})]^{-1}} \tag{36}$$

$$\eta' = \frac{\mu_1 - \mu_2}{\mu_H} \tag{37}$$

$$\sigma' = \frac{1}{T}\frac{\mu_H - \mu_L - (\mu_1 - \mu_2)}{[h_1'(\exp\frac{\mu_H}{kT} - \exp\frac{\mu_1}{kT})]^{-1} + [h_2'(\exp\frac{\mu_2}{kT} - \exp\frac{\mu_L}{kT})]^{-1}} \tag{38}$$

The ecological function of the cycle is

$$E' = P' - T_0\sigma' = \frac{(1+T_0/T)(\mu_1 - \mu_2) - T_0/T(\mu_H - \mu_L)}{[h_1'(\exp\frac{\mu_H}{kT} - \exp\frac{\mu_1}{kT})]^{-1} + [h_2'(\exp\frac{\mu_2}{kT} - \exp\frac{\mu_L}{kT})]^{-1}} \tag{39}$$

Here, one can also introduce a Lagrangian function $L' = E' + \lambda'\eta$, where λ is the Lagrangian multiplier, and from the Euler-Lagrange equations $\partial L' / \partial \mu_1 = 0$ and $\partial L' / \partial \mu_2 = 0$, one can find that the following equation must be satisfied

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$$\frac{\exp\frac{\mu_1}{kT}}{h_1^{'}(\exp\frac{\mu_H}{kT}-\exp\frac{\mu_1}{kT})^2}=\frac{\exp\frac{\mu_2}{kT}}{h_2^{'}(\exp\frac{\mu_2}{kT}-\exp\frac{\mu_L}{kT})^2}=c^{'} \tag{40}$$

Substituting equation (40) into equations (36)-(39) yields the optimal dimensionless ecological function $E^{'*}=E^{'}/(h_1^{'}\mu_H\exp\frac{\mu_H}{kT})$, dimensionless power output $P^{'*}=P^{'}/(h_1^{'}\mu_H\exp\frac{\mu_H}{kT})$, dimensionless entropy production rate $\sigma^{'*}=\sigma^{'}T_0/(h_1^{'}\mu_H\exp\frac{\mu_H}{kT})$ and the efficiency as follows:

$$\begin{aligned}E^{'*}=&\Big[kT\mu_H^{-1}(1+\tfrac{T_0}{T})\ln\Big(y\{\sqrt{b^{'}(1-y)^2y^{-1}\exp\tfrac{\mu_L}{kT}/\exp\tfrac{\mu_H}{kT}+[\tfrac{1}{2}b^{'}(1-y)^2y^{-1}]^2}\\&+\exp\tfrac{\mu_L}{kT}/\exp\tfrac{\mu_H}{kT}+\tfrac{1}{2}b^{'}(1-y)^2y^{-1}\}^{-1}\Big)-\tfrac{T_0}{T}\eta_r\Big]/\Big((1-y)^{-1}+b^{'}\{\tfrac{1}{2}b^{'}(1-y)^2y^{-1}\\&+\sqrt{b^{'}(1-y)^2y^{-1}\exp\tfrac{\mu_L}{kT}/\exp\tfrac{\mu_H}{kT}+[\tfrac{1}{2}b^{'}(1-y)^2y^{-1}]^2}\}^{-1}\Big)\end{aligned} \tag{41}$$

$$\begin{aligned}P^{'*}=&kT\mu_H^{-1}\ln\Big(y\{\sqrt{b^{'}(1-y)^2y^{-1}\exp\tfrac{\mu_L}{kT}/\exp\tfrac{\mu_H}{kT}+[\tfrac{1}{2}b^{'}(1-y)^2y^{-1}]^2}+\exp\tfrac{\mu_L}{kT}/\exp\tfrac{\mu_H}{kT}\\&+\tfrac{1}{2}b^{'}(1-y)^2y^{-1}\}^{-1}\Big)/\Big(b^{'}\{\sqrt{b^{'}(1-y)^2y^{-1}\exp\tfrac{\mu_L}{kT}/\exp\tfrac{\mu_H}{kT}+[\tfrac{1}{2}b^{'}(1-y)^2y^{-1}]^2}\\&+\tfrac{1}{2}b^{'}(1-y)^2y^{-1}\}^{-1}+(1-y)^{-1}\Big)\end{aligned} \tag{42}$$

$$\begin{aligned}\sigma^{'*}=&\tfrac{T_0}{T}\Big[\eta_r-kT\mu_H^{-1}\ln\Big(y\{\sqrt{b^{'}(1-y)^2y^{-1}\exp\tfrac{\mu_L}{kT}/\exp\tfrac{\mu_H}{kT}+[\tfrac{1}{2}b^{'}(1-y)^2y^{-1}]^2}\\&+\exp\tfrac{\mu_L}{kT}/\exp\tfrac{\mu_H}{kT}+\tfrac{1}{2}b^{'}(1-y)^2y^{-1}\}^{-1}\Big)\Big]/\Big((1-y)^{-1}+b^{'}\{\tfrac{1}{2}b^{'}(1-y)^2y^{-1}\\&+\sqrt{b^{'}(1-y)^2y^{-1}\exp\tfrac{\mu_L}{kT}/\exp\tfrac{\mu_H}{kT}+[\tfrac{1}{2}b^{'}(1-y)^2y^{-1}]^2}\}^{-1}\Big)\end{aligned} \tag{43}$$

$$\begin{aligned}\eta^{'}=&kT\mu_H^{-1}\ln\Big(y\exp\tfrac{\mu_H}{kT}\{\sqrt{b\exp\tfrac{\mu_L}{kT}(1-y)^2y^{-1}\exp\tfrac{\mu_H}{kT}+[\tfrac{1}{2}b(1-y)^2y^{-1}\exp\tfrac{\mu_H}{kT}]^2}\\&+\exp\tfrac{\mu_L}{kT}+\tfrac{1}{2}b(1-y)^2y^{-1}\exp\tfrac{\mu_H}{kT}\}^{-1}\Big)\end{aligned} \tag{44}$$

where $y=\exp\frac{\mu_1}{kT}/\exp\frac{\mu_H}{kT}$ and $b^{'}=h_1^{'}/h_2^{'}$. Eliminating $y=\exp\frac{\mu_1}{kT}/\exp\frac{\mu_H}{kT}$ from equations (41)-(44) yields the fundamental optimal relations between the dimensionless ecological function, dimensionless power output, dimensionless entropy production rate and the efficiency of the endoreversible chemical engine with diffusive mass transfer law.

5. Numerical examples and discussion

5.1 Linear mass transfer law

To illustrate the preceding analysis of the cycle with linear mass transfer law, a numerical example is provided. In the calculations, it is set that $\mu_L/\mu_H=0.41$, $b=1.1$, $T_0=300K$, and $T=T_0/1.1$. The numerical values adopted in the calculations were selected. It was not connected to practice. It is for illustrations.

Figure 2 shows the $E^*-\eta$, $P^*-\eta$ and $\sigma^*-\eta$ characteristic of the endoreversible chemical engine with linear mass transfer law. It can be seen from Fig. 2 that the curves of E^* and P^* versus η are parabolic-like ones. The power output has a maxima ($P^*_{\max}$) and the corresponding efficiency is η_{P^*}. The ecological function has also a maxima ($E^*_{\max}$) and the corresponding efficiency is η_{E^*}; the σ decreases as the η increases; the corresponding efficiency η_{E^*} at maximum ecological function is lager than the corresponding efficiency η_{P^*} at maximum power output; the corresponding entropy production rate σ_{E^*} at maximum ecological function is much smaller than the corresponding entropy production rate σ_{P^*} at maximum power output. For this example, one has $P^*_{E^*}/P^*_{\max}=0.728$, $\sigma^*_{E^*}/\sigma^*_{P^*}=0.23$, $\eta_{E^*}/\eta_{P^*}=1.52$. It can be see that taking maximum ecological optimization criterion as the objective makes entropy production rate decreases 77% and efficiency increases 52% with only 27.2% losses of power output.

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The ecological criterion at the maximum power output $E^*_{P^*}$ is far less than the maximum ecological function $E^*_{\max}$. It shows that taking the maximum ecological criterion as objective makes the compromise between the power output and the entropy production rate (exergy loss rate) and this is beneficial to the effective and long-term use of energy.

Figure 3 shows the influence of mass-reservoir chemical potential ratio μ_L / μ_H on the ecological function versus the efficiency characteristic. It can be seen that with the increases of mass-reservoir chemical potential ratio, both the ecological function and the corresponding efficiency decrease.

Figure 4 shows the influence of mass-transfer coefficient ratio b on the ecological function versus the efficiency characteristic. It can be seen that with the increases of b, the ecological function decreases for the same efficiency.

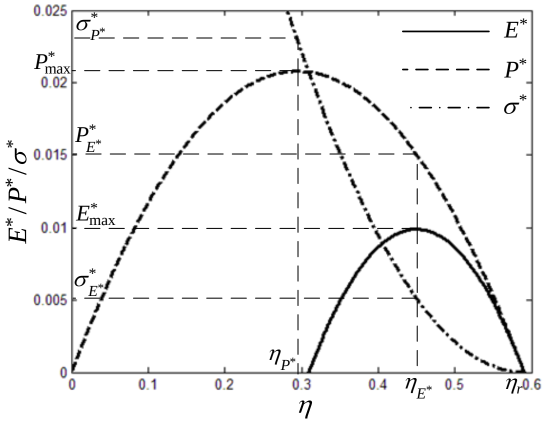

Figure 2. $E^* - \eta$, $P^* - \eta$ and $\sigma^* - \eta$ characteristic of an endoreversible chemical engine with linear mass transfer law

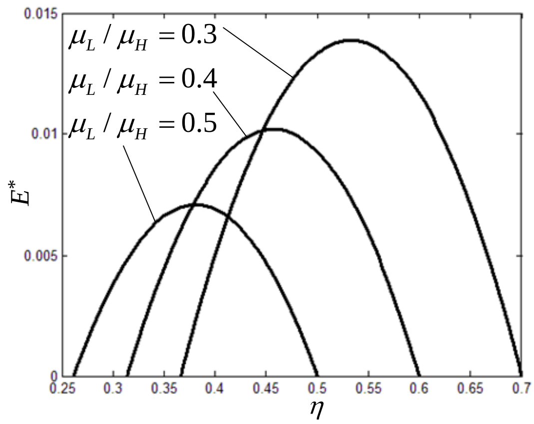

Figure 3. The influence of μ_L / μ_H on E^* versus η

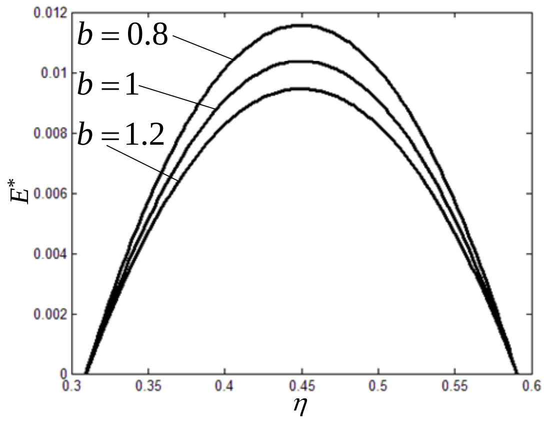

Figure 4. The influence of b on E^* versus η

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5.2 Diffusive mass transfer law

To illustrate the preceding analysis of cycle with diffusive mass transfer law, a numerical example is provided. In the calculations, it is set that $\exp\frac{\mu_L}{kT}=4$, $\exp\frac{\mu_L}{kT}/\exp\frac{\mu_H}{kT}=\exp(-\frac{\mu_H-\mu_L}{kT})=\exp(-2)$, $b^{'}=1.1$, $T_0=300K$, and $T=T_0/1.1$.

Figure 5 shows the $E^{'*}-\eta^{'}$, $P^{'*}-\eta^{'}$ and $\sigma^{'*}-\eta^{'}$ characteristic of the endoreversible chemical engine with diffusive mass transfer law. It can be seen from Fig. 5 that the curves of $E^{'*}$ and $P^{'*}$ versus $\eta^{'}$ are also parabolic-like ones as that of linear mass transfer law. But with the same values of μ_H and μ_L, the result is different. For this example, one has $P^{'*}_{E^*}/P^{'*}_{\max}=0.693$, $\sigma^{*'}_{E^*}/\sigma^{*'}_{P^*}=0.2$, $\eta^{'}_{E^*}/\eta^{'}_{P^*}=1.645$ and $E^{'*}_{\max}=0.0112$. It can be see that taking maximum ecological optimization criterion as the objective makes entropy production rate decreases 80% and efficiency increases 64.5% with only 30.7% losses of power output.

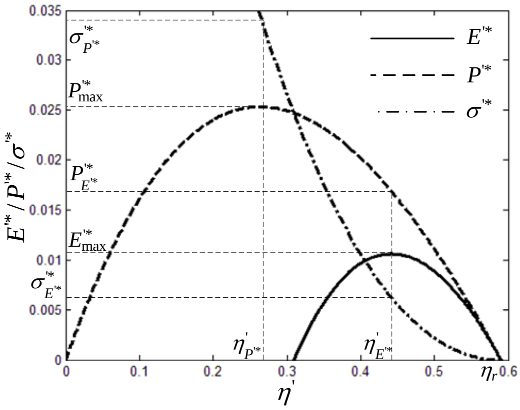

Figure 5. $E^{'*}-\eta^{'}$, $P^{'*}-\eta^{'}$ and $\sigma^{'*}-\eta^{'}$ characteristic of an endoreversible chemical engine with diffusive mass transfer law

Figure 6 shows the influence of $(\mu_H-\mu_L)/kT$ on the ecological function versus the efficiency characteristic of the cycle with diffusive mass transfer law. It can be seen that with the increases of mass-reservoir chemical potential ratio, the maximum ecological function increases first but then decreases. And the corresponding efficiency increases.

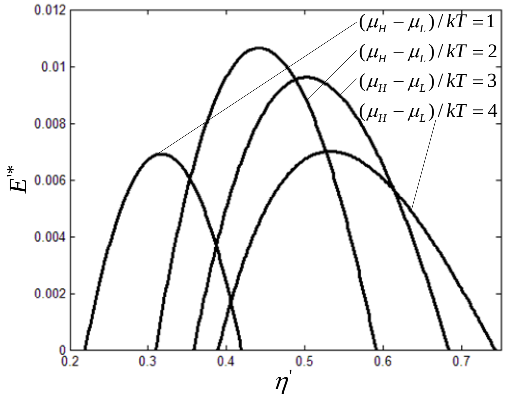

Figure 6. The influence of $(\mu_H-\mu_L)/kT$ on $E^{'*}$ versus $\eta^{'}$

Figure 7 shows the influence of mass-transfer coefficient ratio $b^{'}$ on the ecological function versus the efficiency characteristic of the cycle with diffusive mass transfer law. It can be seen that with the increases of $b^{'}$, the ecological function decreases for the same efficiency.

Figure 8 shows the influence of mass transfer law on dimensionless ecological function versus efficiency. It can be seen that the maximum ecological function with linear mass transfer law $E^{*}_{\max}$ is smaller than that of diffusive mass transfer law $E^{'*}_{\max}$, while the corresponding efficiency with linear mass transfer law η_{E^*} is much bigger than that of diffusive mass transfer law $\eta^{'}_{E^{'*}}$.

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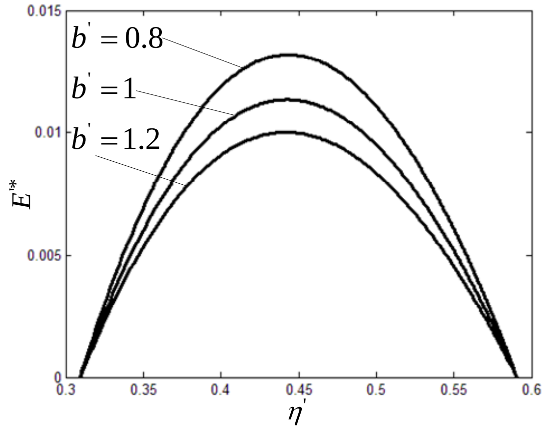

Figure 7. The influence of b' on E'^* versus η'

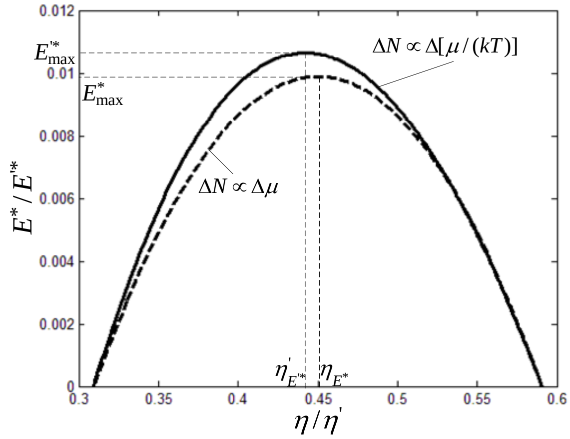

Figure 8. The influence of mass transfer law on dimensionless ecological function versus efficiency

5.3 Comparison between power output and ecological function for chemical engine

Whenever the chemical engine obeys linear or nonlinear mass transfer law, the optimization of the ecological function makes the entropy-generation rate of the cycle decrease greatly and the efficiency increase with little decrease of the power output. So it represents not only a compromise between the power output and the entropy-generation rate but also one between the power output and the efficiency, and this is beneficial to the effective and long-term use of energy.

5.4 Comparison between chemical engine and heat engine

Angulo-Brown et al. concluded that $P_E / P_{\max} = 0.75$ and $\sigma_E / \sigma_P = 0.25$ always hold for endoreversible [18] and non-endoreversible [19] heat-engines. However, taking $E' = P - T_L\sigma$ as the optimal function, the results of this paper show that $P^*_{E^*} / P^*_{\max} = 0.75$ and $\sigma^*_{E^*} / \sigma^*_{P^*} = 0.25$ for an endoreversible chemical engine with linear mass transfer law, which has the same regulation with that of heat engine. But if taking $E = P - T_0\sigma$ as the optimal function, or consider the cycle with diffusive mass transfer law, they would have different results, as shown in Table 1.

Table 1. Comparison for different optimization results

	$\Delta N \propto \Delta\mu$		$\Delta N \propto \Delta(\mu / kT)$	
	$T = T_0$	$T_0 / T = 1.1$	$T = T_0$	$T_0 / T = 1.1$
$P^*_E / P^*_{\max}$	0.75	0.728	0.693	0.667
$\sigma^*_{E^*} / \sigma^*_{P^*}$	0.25	0.23	0.2	0.182
η_{E^*} / η_{P^*}	1.5	1.52	1.645	1.67

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6. Conclusion

In this paper, the relations between the ecological function, power output, entropy production rate and the efficiency of an endoreversible chemical engine cycle with both linear and nonlinear mass transfer laws are derived. The maximum ecological function and the corresponding power output, efficiency, and entropy production rate, and the maximum power output and the corresponding ecological function, efficiency, and entropy production rate are also derived. Two numerical examples are provided. Taking an ecological optimization criterion as the objective, it sacrifices a little part of the power output, decreases the entropy production rate to a great extent and increases the efficiency to some extent. The ecological criterion reflects a compromise between the power output and the entropy production rate for endoreversible chemical engines, as well as a compromise between the power output and the efficiency, and it is a candidate objective having long-term meaning for optimal design of chemical engines. The results obtained herein may be used in the design of mass exchangers, electrochemical, fuel pumps, photochemical and solid state devices, and so on. This can provide some new theoretical instructions for the optimal design of these devices.

The further assumption by adding irreversibilities due to mass leakage and internal source of irreversibility is necessary. The analysis of chemical engines operating with both temperature and chemical potential differences, and for an arbitrary number of chemical components is also necessary. They will be the subjects of a further presentation.

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Nomenclature

b	The mass-transfer coefficient ratio
E	The ecological function
h	The mass-transfer coefficient
k	Boltzmann's constant
L	Lagrangian function
P	The power output (kJ/s)
T	Temperature (K)
t	Mass-transfer time (s)
τ	The cyclic period (s)
ΔN	The amounts of mass exchange per cycle (kg)
ΔS	The entropy generation per cycle $((kW \cdot s)/K)$

Greek symbol

η	The efficiency
λ	Lagrangian multiplier
μ	Chemical potential (kJ/kg)
σ	The entropy production rate (kW/K)

Subscripts

*	dimensionless
E	The maximum ecological function point
H	The high mass-reservoir
L	The low mass-reservoir
max	Maximum
P	The maximum power output point
r	Reversible cycle
1,2	State points
'	with diffusive mass transfer law

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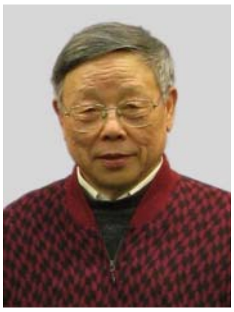

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