SCIENCE CHINA
Chemistry

• ARTICLES •

May 2010 Vol.53 No.5: 1168–1176
doi: 10.1007/s11426-010-0132-x

Maximum work configurations of finite potential capacity reservoir chemical engines

XIA ShaoJun, CHEN LinGen* & SUN FengRui

Postgraduate School, Naval University of Engineering, Wuhan 430033, China

Received June 12, 2009; accepted July 27, 2009

An isothermal endoreversible chemical engine operating between the finite potential capacity high-chemical-potential reservoir and the infinite potential capacity low-chemical-potential reservoir has been studied in this work. Optimal control theory was applied to determine the optimal cycle configurations corresponding to the maximum work output per cycle for the fixed total cycle time and a universal mass transfer law. Analyses of special examples showed that the optimal cycle configuration with the mass transfer law $g \propto \Delta\mu$, where $\Delta\mu$ is the chemical potential difference, is an isothermal endoreversible chemical engine cycle, in which the chemical potential (or the concentration) of the key component in the working substance of low-chemical-potential side is a constant, while the chemical potentials (or the concentrations) of the key component in the finite potential capacity high-chemical-potential reservoir and the corresponding side working substance change nonlinearly with time, and the difference of the chemical potentials (or the ratio of the concentrations) of the key component between the high-chemical-potential reservoir and the working substance is a constant. While the optimal cycle configuration with the mass transfer law $g \propto \Delta c$, where Δc is the concentration difference, is different from that with the mass transfer law $g \propto \Delta\mu$ significantly. When the high-chemical-potential reservoir is also an infinite potential capacity chemical potential reservoir, the optimal cycle configuration of the isothermal endoreversible chemical engine consists of two constant chemical potential branches and two instantaneous constant mass-flux branches, which is independent of the mass transfer law. The object studied in this paper is general, and the results can provide some guidelines for optimal design and operation of real chemical engines.

isothermal endoreversible chemical engine, maximum work output, optimal control, finite time thermodynamics, generalized thermodynamic optimization

1 Introduction

There are two standard problems in finite time thermodynamics. One is to determine the objective function limits and the relations between objective functions for the given thermodynamic system, and another is to determine the optimal thermodynamic process for the given optimization objectives [1–10]. Curzon and Ahlborn [11] postulated a Carnot engine with power output limited by the rates of heat transfer to and from the working fluid, and showed that the hot- and cold-end temperature of a power plant can be optimized so that the power output is maximum. The efficiency at maximum power point is $\eta_{CA} = 1 - \sqrt{T_{\mathrm{L}} / T_{\mathrm{H}}}$. Procaccia and Ross [12] proved that in all acceptable cycles, an endoreversible Carnot cycle with larger compression ratio can produce maximum power, i.e., the Curzon-Ahlborn (CA) cycle [11] is the optimal configuration with only First and Second Law constraints. Ondrechen *et al.* [13] investigated the problem of maximizing work output from a finite thermal capacity heat reservoir by infinite sequential Carnot cycles. Ondrechen *et al.* [14] further investigated the optimal configuration of reciprocating heat engine operating between a finite thermal capacity high-temperature heat reservoir and an infinite thermal capacity low-temperature

---

*Corresponding author (email: lgchenna@yahoo.com, lingenchen@hotmail.com) heat reservoir for maximum work output per cycle. Amelkin *et al.* [15, 16] investigated the optimal configuration of an endoreversible heat engine with several infinite thermal capacity heat reservoirs for maximum power output. Sieniutycz and von Sparkovsky [17] obtained the optimal reservoir temperature profiles of multistage continuous CA heat engine systems operating between finite thermal capacity high-temperature heat reservoir and infinite thermal capacity low-temperature heat reservoir for maximum work output, and further obtained those of multistage discrete heat engine systems for maximum work output [18].

The idea and method of finite time thermodynamic optimization for heat engines can be extended to generalized thermodynamic processes and devices. De Vos [19–22] has extended the definition of the endoreversible heat engine to a generalized endoreversible engine by generalizing heat reservoir to heat and mass reservoir and heat exchanger to heat and mass exchanger, and investigated the finite-time-thermodynamic performances of solar energy conversion processes and devices with finite temperature difference heat transfer and finite chemical potential difference mass transfer, such as chemical reactions and solar energy cells. Tsirlin *et al.* [23] analyzed the performance of chemical reactors. Gordon [24] investigated the problem of maximizing work output from a finite potential capacity chemical potential reservoir by infinite sequential isothermal chemical engines. Gordon and Orlov [25] further investigated the optimal configuration of isothermal endoreversible chemical engine operating between two chemical potential reservoirs for maximum average power output, and found that the optimal cycle configuration of isothermal endoreversible chemical engine with infinite potential capacity chemical potential reservoirs consisted of two constant chemical potential branches and two instantaneous constant mass-flux branches, which is similar to the CA cycle [11] for the heat engine. The optimal cycle configuration of endoreversible chemical engine with finite potential capacity chemical potential reservoirs was also discussed qualitatively in ref. [25]. Chen *et al.* [6, 26–28] derived the optimal relation between the power output and the second law efficiency of both the isothermal endoreversible simple chemical engine and the combined-cycle isothermal endoreversible chemical engines, and analyzed the effect of mass leakage on the performance of isothermal chemical engines [6, 29]. Lin *et al.* [30] investigated effects of mass transfer, mass leakage and internal irreversibility on the performance of isothermal chemical engines. Tsirlin *et al.* [31] also derived the minimum entropy generation of a class of chemical engines. Chen *et al.* [32] investigated effects of mass transfer laws on the performance of isothermal endoreversible chemical engines. Sieniutycz [33–35] analyzed the optimal performance of multistage continuous chemical engine systems with simultaneous heat and mass transfer by applying HJB (Hamilton-Jacobi-Bellman) equations. Xia *et al.* [36] derived the optimal cycle configuration of a multi-reservoir isothermal endoreversible chemical engine with the linear mass transfer law [$g \propto \Delta\mu$] for maximum work output. The previous work has focused on investigating optimal performances [19–22, 24, 26–35] and optimal configurations [22, 31, 36] of isothermal chemical engines with infinite potential capacity chemical potential reservoirs. The optimal cycle configuration of an isothermal endoreversible chemical engine with finite chemical-potential reservoirs was discussed qualitatively in ref. [25], but the model of the finite potential capacity chemical potential reservoir wasn't described in detail and the results obtained in ref. [25] didn't reflect the essence of optimal cycle configuration of the isothermal endoreversible chemical engine with finite potential capacity chemical potential reservoirs. Heat transfer laws have significantly effects on the optimal cycle configurations of heat engines with finite thermal capacity heat reservoirs [37–42]. In the same manner, mass transfer laws have significant effects on the optimal cycle configurations of isothermal endoreversible chemical engines with finite potential capacity chemical potential reservoirs. One of the aims of finite time thermodynamics is to pursue generalized rules and results. This paper will further derive the optimal cycle configurations of isothermal endoreversible chemical engines operating between finite potential capacity high-chemical-potential reservoirs and infinite potential capacity low-chemical-potential reservoirs for maximum work output per cycle by using a universal mass transfer law.

2 Physical model

The isothermal endoreversible chemical engine model to be considered in this paper is shown in Figure 1. It operates between a finite potential capacity high-chemical-potential

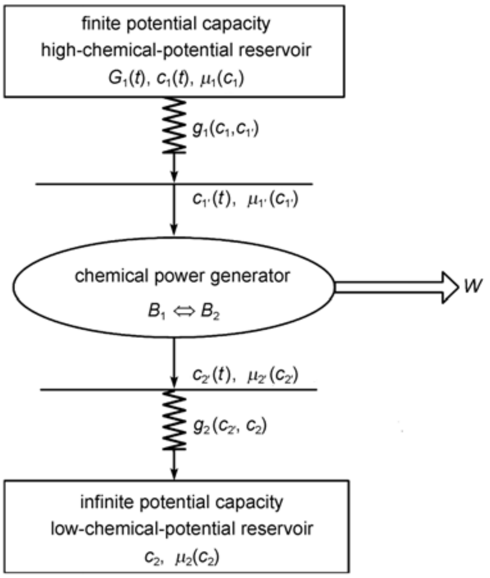

Figure 1 Model of the isothermal endoreversible chemical engine.

reservoir and an infinite potential capacity low-chemical-potential reservoir. The total mass of the material in the high-chemical-potential reservoir is given by $G_1(t)$. At initial time $t=0$, $G_1(0)=G_{10}$. The high-chemical-potential reservoir is a finite potential reservoir, so the chemical potential of the key component B_1 in it will change during the mass-absorbing process of the working substance in the chemical engine. The concentration (mole fraction) and the chemical potential of the key component B_1 in the high-chemical-potential reservoir are set to be $c_1(t)$ and $\mu_1(c_1)$, respectively. The chemical reaction in the chemical engine is assumed to be a single reversible isomerisation reaction $B_1 \Leftrightarrow B_2$. The amount of heat absorbed or released due to the chemical reaction is so small that it could be neglected, so the temperature over the cycle process is a constant. The concentration and the chemical potential of the key component B_1 in the working substance of the chemical engine at the high-chemical-potential side are given by $c_{1'}(t)$ and $\mu_{1'}(c_{1'})$, respectively, while those of the key component B_2 at the low-chemical-potential side are given by $c_{2'}(t)$ and $\mu_{2'}(c_{2'})$, respectively. The low-chemical -potential reservoir is an infinite potential capacity chemical potential reservoir, so both the concentration and the chemical potential of the key component B_2 in it are constants and are given by c_2 and $\mu_2(c_2)$, respectively. The chemical engine receives its mass N_1 from the high-chemical-potential reservoir, and rejects its mass N_2 to the low-chemical-potential reservoir over the cycle time. The chemical engine operates in a cyclic fashion with a fixed time τ allotted for each cycle. Then eqs. (1) and (2) are obtained as follows.

$$N_1 = \int_0^\tau g_1\left(c_1(t), c_{1'}(t)\right)\mathrm{d}t \tag{1}$$

$$N_2 = \int_0^\tau g_2\left(c_{2'}(t), c_2(t)\right)\mathrm{d}t \tag{2}$$

where $g_1(c_1(t),c_{1'}(t))$ and $g_2(c_{2'}(t),c_2(t))$ are mass flow rates corresponding to the high- and low-chemical-potential sides, respectively. The law of mass conservations gives $N_1=N_2$, i.e.,

$$\int_0^\tau g_1\left(c_1(t), c_{1'}(t)\right)\,\mathrm{d}t - \int_0^\tau g_2\left(c_{2'}(t), c_2(t)\right)\,\mathrm{d}t = 0 \tag{3}$$

From the first law of thermodynamics, the equation of energy conservation over the total cycle is

$$\int_0^\tau \left[U_1(t) - U_2(t)\right]\,\mathrm{d}t - \int_0^\tau P(t)\,\mathrm{d}t = 0 \tag{4}$$

where $U_1(t)$ and $U_2(t)$ are the total energy flow rates at high- and low-chemical-potential sides of the working substance in the chemical engine, respectively. $P(t)$ is the instantaneous power output of the chemical engine. In terms of the second law of thermodynamics, the entropy change of the working substance in the isothermal endoreversible chemical engine for the whole cycle is zero, i.e., the entropy flux input is equal to the entropy flux output:

$$\left\{\int_0^\tau \left[U_1(t) - g_1(c_1, c_{1'})\mu_{1'}(c_{1'})\right]\,\mathrm{d}t - \int_0^\tau \left[U_2(t) - g_2(c_{2'}, c_2)\mu_{2'}(c_{2'})\right]\,\mathrm{d}t\right\}\Big/ T = 0 \tag{5}$$

where T is the temperature during mass transfer processes, which is a constant. The work output per cycle (W) is obtained by combining eq. (4) with eq. (5) as follows:

$$\begin{aligned} W &= \int_0^\tau P(t)\,\mathrm{d}t \\ &= \int_0^\tau \left[g_1(c_1, c_{1'})\mu_{1'}(c_{1'}) - g_2(c_{2'}, c_2)\mu_{2'}(c_{2'})\right]\,\mathrm{d}t \end{aligned} \tag{6}$$

For the high-chemical-potential reservoir, the total mass ($G_1(t)$) versus time obeys the following differential equation:

$$\frac{\mathrm{d}G_1}{\mathrm{d}t} = -g_1(c_1, c_{1'}), \quad G_1(0) = G_{10} \tag{7}$$

Considering that there is a transfer of the key component B_1 only between the high-chemical-potential reservoir and the working substance in the chemical engine, then eq. (8) is obtained as follows:

$$\frac{\mathrm{d}(G_1 c_1)}{\mathrm{d}t} = \frac{\mathrm{d}G_1}{\mathrm{d}t} \tag{8}$$

From eqs. (7) and (8), eq. (9) is obtained as follows:

$$\frac{\mathrm{d}c_1}{\mathrm{d}t} = -\frac{(1-c_1)}{G_1} g_1(c_1, c_{1'}) \tag{9}$$

The total mass of the inert component in the mixture of high-chemical-potential reservoir is a constant during the finite rate mass transfer process, i.e.

$$G_1(1-c_1) = \hat{G} \tag{10}$$

where $\hat{G} = G_{10}(1-c_{10})$ is a constant. Substituting eq. (10) into eq. (9) yields:

$$\dot{c}_1 = -\frac{(1-c_1)^2}{\hat{G}} g_1(c_1, c_{1'}) \tag{11}$$

where $\dot{c}_1 = \mathrm{d}c_1/\mathrm{d}t$.

3 Optimization

The problem now is to maximize the work output of the isothermal endoreversible chemical engine for the fixed duration τ, i.e., to determine the optimal time paths of parameters $c_1(t)$, $c_{1'}(t)$ and $c_{2'}(t)$ for the maximum W of eq. (6) subjected to the constraints of eqs. (3) and (11). Apparently, it is a typical optimal control problem. One could solve

Euler-Lagrange equations for the optimal solutions by constructing a modified Lagrange function. For the peculiarity of the optimization problem considered here, the solving process could be simplified by transforming this optimal control problem to a class of average optimal control problems, which include two sub-problems [2]:

Problem 1: When $0 \leqslant t \leqslant t_1$, the constraints of the problem are given by

$$\int_0^{t_1} g_1\left(c_1(t), c_{1'}(t)\right) \mathrm{d}t = N_1 \tag{12}$$

$$\hat{G}\dot{c}_1 = -\left(1-c_1\right)^2 g_1\left(c_1, c_{1'}\right) \tag{13}$$

The problem is to determine the maximum value of the following objective function,

$$\max \quad W^+ = \int_0^{t_1} g_1\left(c_1, c_{1'}\right) \mu_{1'}\left(c_{1'}\right) \mathrm{d}t \tag{14}$$

Problem 2: When $t_1 \leqslant t \leqslant \tau$, the constraint of the problem is given by

$$\int_{t_1}^{\tau} g_2\left(c_{2'}(t), c_2(t)\right) \mathrm{d}t = N_2 \tag{15}$$

The problem is to determine the maximum value of the following objective function,

$$\max \quad W^- = \int_{t_1}^{\tau} -g_2\left(c_{2'}, c_2\right) \mu_{2'}\left(c_{2'}\right) \mathrm{d}t \tag{16}$$

For problem 1, eq. (13) further gives

$$\int_{c_{10}}^{c_1(t_1)} \frac{-\hat{G}}{g_1\left(c_1, c_{1'}\right)\left(1-c_1\right)^2} \mathrm{d}c_1 = t_1 \tag{17}$$

Substituting eq. (13) into eqs. (12) and (14), separately, yields

$$\int_{c_{10}}^{c_1(t_1)} -\frac{\hat{G}}{\left(1-c_1\right)^2} \mathrm{d}c_1 = N_1 \tag{18}$$

$$\max \quad W^+ = \int_{c_{10}}^{c_1(t_1)} -\frac{\hat{G}}{\left(1-c_1\right)^2} \mu_{1'}\left(c_{1'}\right) \mathrm{d}c_1 \tag{19}$$

Problem 1 now is to maximize W^+ of eq. (19) subjected to the constraints of eqs. (17) and (18). Apparently, it is a typical average optimal control problem in optimal control theory. Correspondingly, the modified Lagrangian L is given by

$$L = -\frac{\hat{G}}{\left(1-c_1\right)^2}\left[\mu_{1'}\left(c_{1'}\right) + \frac{\lambda_1}{g_1\left(c_1, c_{1'}\right)} + \lambda_2\right] \tag{20}$$

where λ_1 and λ_2 are the Lagrangian multipliers, and they are constants to be determined. From the extreme condition $\partial L/\partial c_{1'} = 0$, one can obtain

$$\frac{\partial \mu_{1'}}{\partial c_{1'}} - \frac{\lambda_1}{g_1^2\left(c_1, c_{1'}\right)} \frac{\partial g_1}{\partial c_{1'}} = 0 \tag{21}$$

According to ref. [31], the chemical potential μ_i of the i-th component in ideal mixture which is similar in properties to ideal gases or ideal solutions can be expressed as

$$\mu_i\left(c_i\right) = \mu_{0i}\left(P, T\right) + RT \ln c_i, \quad i = 1,\ 1',\ 2',\ 2 \tag{22}$$

where c_i is the concentration of the i-th component, P and T are the mixture's absolute temperature and pressure, R is the universal gas constant, and $\mu_{0i}(P,T)$ is the chemical potential of the pure i-th component (known for most of substances). From eq. (22), one can obtain $\partial \mu_{1'}/\partial c_{1'} = (RT)/(c_{1'})$. Substituting it into eq. (21) yields

$$\frac{\partial g_1}{\partial c_{1'}} = \frac{RT}{\lambda_1 c_{1'}} g_1^2\left(c_1, c_{1'}\right) \tag{23}$$

Problem 2 is also an average optimal control problem. Correspondingly, the modified Lagrangian L is given by

$$L = -g_2\left(c_{2'}, c_2\right)\mu_{2'}\left(c_{2'}\right) + \lambda g_2\left(c_{2'}, c_2\right) \tag{24}$$

where λ is the Lagrangian multiplier, and it is a constant to be determined. From the extreme condition $\partial L/\partial c_{2'} = 0$, one can obtain

$$\frac{\partial g_2}{\partial c_{2'}}\left(\mu_{2'} + \lambda\right) + g_2\left(c_{2'}, c_2\right)\frac{\partial \mu_{2'}}{\partial c_{2'}} = 0 \tag{25}$$

From eq. (22), one can also obtain $\partial \mu_{2'}/\partial c_{2'} = (RT)/(c_{2'})$. Substituting it into eq. (25) yields

$$\frac{\partial g_2}{\partial c_{2'}} = \frac{RT g_2\left(c_{2'}, c_2\right)}{\left(\mu_{2'} + \lambda\right) c_{2'}} \tag{26}$$

For the given type of the mass transfer laws $g_1(c_1, c_{1'})$ and $g_2(c_{2'}, c_2)$, the optimal configurations of the mass transfer processes corresponding to the high- and the low-chemical-potential sides of the chemical engine can be obtained from eqs. (21) and (26).

4 Analyses for special examples and discussion

4.1 The case with the mass transfer law $g \propto \Delta\mu$ and a finite potential capacity high-chemical-potential reservoir

Considering that the mass transfers at the high- and low-chemical potential sides obey the mass transfer law $g \propto \Delta\mu$ in Onsager's linear irreversible thermodynamics, the mass flow rates $g_1(c_1(t), c_{1'}(t))$ and $g_2(c_{2'}(t), c_2(t))$ are, respectively, given by

$$g_1\left(c_1(t), c_{1'}(t)\right) = h_1(t)\left[\mu_1\left(c_1\right) - \mu_{1'}\left(c_{1'}\right)\right] \tag{27}$$

$$g_2\left(c_{2'}(t), c_2(t)\right) = h_2(t)\left[\mu_{2'}\left(c_{2'}\right) - \mu_2\left(c_2\right)\right] \tag{28}$$

where $h_1(t)$ and $h_2(t)$ are the corresponding mass- transfer coefficients, respectively. It is assumed that at $t = 0$ the working substance is in contact with high- chemical-potential reservoir and is separated from the low-chemical-potential reservoir by an instantaneous constant mass-flux branch. At a later time t_1 $(0 < t_1 < \tau)$, contact with the high-chemical-potential reservoir is broken and the working substance is placed in contact with the low-chemical-potential reservoir. Therefore, one has the following relationships:

$$h_1(t) = \begin{cases} h_1, & 0 \leqslant t \leqslant t_1 \\ 0, & t_1 \leqslant t \leqslant \tau \end{cases}, \quad h_2(t) = \begin{cases} 0, & 0 \leqslant t \leqslant t_1 \\ h_2, & t_1 \leqslant t \leqslant \tau \end{cases} \tag{29}$$

where h_1 and h_2 are constants, and t_1 is the time spent on the mass-absorbing process. From eq. (27), one can obtain $\partial g_1/\partial c_{1'} = -h_1 \partial \mu_{1'}/\partial c_{1'}$. Substituting it into eq. (21) yields:

$$g_1\left(c_1, c_{1'}\right) = \text{const} \tag{30}$$

Eq. (30) shows that the mass flow rate during the mass transfer process is a constant when the chemical engine is in contact with the high-chemical-potential reservoir. Substituting eq. (27) into eq. (30) yields

$$\mu_1 - \mu_{1'} = C_\mu, \quad 0 \leqslant t \leqslant t_1 \tag{31}$$

where C_μ is an integration constant. Eq. (31) shows that the chemical potential difference of the key component B_1 between the high-chemical-potential reservoir and the working substance is a constant when working substance of the chemical engine is in contact with the high-chemical-potential reservoir. Substituting eq. (22) into eq. (31) yields

$$c_1(t)/c_{1'}(t) = \exp\left(C_\mu/RT\right) \tag{32}$$

Eq. (32) shows that the ratio of the concentration of the key component B_1 in the high-chemical-potential reservoir to that in the working substance of the chemical engine is a constant for the optimal cycle configuration. From eq. (28), one can obtain $\partial g_2/\partial c_{2'} = h_2 \partial \mu_{2'}/\partial c_{2'}$. Substituting it and eq. (28) into eq. (25) yields

$$\mu_{2'} = \left(\mu_2 - \lambda\right)/2, \quad t_1 \leqslant t \leqslant \tau \tag{33}$$

where both μ_2 and λ are constants. Eq. (33) shows that the chemical potential $(\mu_{2'})$ of the key component B_2 in the working substance is also a constant when the working substance of chemical engine is in contact with the infinite potential capacity low-chemical-potential reservoir. The inequality $\mu_{2'} > \mu_2$ holds during the mass transfer process between the chemical engine and the low-chemical-potential reservoir, so $\lambda < 0$ is obtained from eq. (33). The concentration $(c_{2'})$ of the key component B_2 in the working substance is also a constant due to that the equation $\mu_{2'} = \mu_{02} + RT\ln(c_{2'})$ holds. The total mass $(G_1(t))$ of the material in the high-chemical-potential reservoir versus time is obtained by substituting eqs. (27) and (31) into eq. (7), i.e.,

$$G_1(t) = G_1(0) - h_1 C_\mu t \tag{34}$$

Substituting eq. (34) into eq. (9) yields

$$\frac{\mathrm{d}c_1}{\mathrm{d}t} = -\frac{\left(1 - c_1\right)}{G_{10} - h_1 C_\mu t} h_1 C_\mu, \quad c_1(0) = c_{10} \tag{35}$$

The concentration $(c_1(t))$ of the key component B_1 in the high-chemical-potential reservoir versus time is obtained from eq. (35), i.e.,

$$c_1(t) = 1 - \left(1 - c_{10}\right)\frac{G_{10}}{G_{10} - h_1 C_\mu t} \tag{36}$$

The concentration $(c_{1'}(t))$ of the key component B_1 in the working substance of the chemical engine versus time during the mass-absorbing process is obtained by substituting eq. (36) into eq. (32), which is given by

$$c_{1'}(t) = \left[1 - G_{10}\left(1 - c_{10}\right)/\left(G_{10} - h_1 C_\mu t\right)\right]/\exp\left(C_\mu/RT\right) \tag{37}$$

The concentration $(c_{2'})$ of the key component B_2 in the working substance of the chemical engine during the mass-releasing process is obtained by combining eqs. (3), (28) with eq. (31), which is given by

$$c_{2'} = c_2 \exp\left\{h_1 C_\mu t_1/\left[h_2 RT\left(\tau - t_1\right)\right]\right\} \tag{38}$$

From eq. (38), $c_{2'}$ is a constant to be determined, which is related to the values of the mass-absorbing process time t_1 and the integration constant C_μ. The work output (W) per cycle is obtained by combining eq. (6) with eqs. (36)–(38), which is given by

$$\begin{aligned} W = RT\Bigg[& h_1 C_\mu t_1 \ln\left(\frac{G_{10}c_{10} - h_1 C_\mu t_1}{G_{10} - h_1 C_\mu t_1}\right) + G_{10}\ln\left(\frac{G_{10} - h_1 C_\mu t_1}{G_{10}}\right) \\ & - G_{10}c_{10}\ln\left(\frac{G_{10}c_{10} - h_1 C_\mu t_1}{G_{10}c_{10}}\right)\Bigg] + h_1 C_\mu t_1\left(\Delta\mu_0 - RT\ln c_2\right) \\ & - h_1 C_\mu{}^2 t_1 \frac{h_2\left(\tau - t_1\right) + h_1 t_1}{h_2\left(\tau - t_1\right)} \end{aligned} \tag{39}$$

where $\Delta\mu_0 = \mu_{01} - \mu_{02}$, μ_{01} and μ_{02} are chemical potentials of the pure substances B_1 and B_2, respectively.

For the given values of parameters G_{10}, c_{10}, h_2, $\Delta\mu_0$ and T, the work output (W) per cycle is a function of the integration constant C_μ and the time t_1. One cannot obtain the analytical solutions from the extreme conditions $\partial W/\partial t_1 = 0$ and $\partial W/\partial C_\mu = 0$, which can only be solved numerically. The optimal cycle configuration of the chemical engine operating between a finite potential capacity high-chemical-potential reservoir and an infinite potential capacity low-chemical -potential reservoir with the mass transfer law $g \propto \Delta\mu$ for maximum work output is an isothermal endoreversible chemical engine cycle in which the chemical potential (or the concentration) of the key component in the working substance of low-chemical-potential side is a constant, while the chemical potentials (or the concentrations) of the key component in the finite potential capacity high-chemical-potential reservoir and the corresponding side working substance change nonlinearly with time, and the difference of the chemical potentials (or the ratio of the concentrations) of the key component between the high-chemical-potential reservoir and the working substance is a constant.

4.2 The case with the mass transfer law $g \propto \Delta\mu$ and an infinite potential capacity high-chemical-potential reservoir

The initial mass is $G_{10}\to\infty$ when the high-chemical-potential reservoir is an infinite potential capacity chemical potential reservoir. From eq. (36), it can be concluded that the concentration ($c_1(t)$) of the key component B_1 in the high-chemical-potential reservoir is equal to its initial concentration c_{10}.The chemical potential μ_1 is a constant because equation $\mu_1=\mu_{01}+RT\ln c_1$ holds. The chemical potential ($\mu_{1'}$) of the key component B_1 in the working substance of the chemical engine is also a constant from eq. (31). Now, the optimal cycle configuration consists of two constant chemical potential branches and two instantaneous constant mass-flux branches, which is analogous to the CA cycle [11] for the heat engine. This is the same result as that obtained in refs. [25, 31]. The corresponding average power output $\bar{P}$ and the second law efficiency η are

$$\bar{P}=W/\tau=\left(\mu_{1'}-\mu_{2'}\right)N_1/\tau \tag{40}$$

$$\eta=\frac{W}{W_{rev}}=\frac{\left(\mu_{1'}-\mu_{2'}\right)N_1}{\left(\mu_1-\mu_2\right)N_1}=\frac{\mu_{1'}-\mu_{2'}}{\mu_1-\mu_2} \tag{41}$$

Combining eqs. (1), (2), (40) with eq. (41) yields

$$\bar{P}=\frac{\eta\left(1-\eta\right)\left(\mu_1-\mu_2\right)^2}{\tau\left\{\left(h_1t_1\right)^{-1}+\left[h_2\left(\tau-t_1\right)\right]^{-1}\right\}} \tag{42}$$

where $t_1=\tau/[1+(h_1/h_2)^{0.5}]$ is obtained from the extreme condition $\partial\bar{P}/\partial t_1=0$, and the corresponding optimal power versus efficiency is given by

$$\bar{P}=\frac{h_1\eta\left(1-\eta\right)\left(\mu_1-\mu_2\right)^2}{\left[1+\left(h_1/h_2\right)^{0.5}\right]^2} \tag{43}$$

This is the same result as that obtained in ref. [26]. Eq. (43) shows that the optimal power versus efficiency of the isothermal endoreversible chemical engine operating between two infinite potential capacity chemical potential reservoirs is a parabolic-like curve, which is analogous to that for the endoreversible heat engine operating between two infinite thermal capacity heat reservoirs [1–5, 11]. Also from eq. (43), one can obtain $\bar{P}=0$ when $\eta=\eta_{\min}=0$ and $\eta=\eta_{\max}=1$ and the average power output attains its maximum $\bar{P}_{\max}=\dfrac{h_1(\mu_1-\mu_2)^2}{4[1+(h_1/h_2)^{0.5}]^2}$ when $\eta=\eta_P=0.5=\eta_{\max}/2$.

4.3 The case with the mass transfer law $g\propto\Delta c$ and a finite potential capacity high-chemical -potential reservoir

Considering that the mass transfers at the high- and low-chemical potential sides obey another linear mass transfer law [$g \propto \Delta(c)$] [33–35], then the mass flow rates $g_1(c_1(t),c_{1'}(t))$ and $g_2(c_{2'}(t),c_2(t))$ are respectively given by

$$\begin{aligned}g_1\left(c_1(t),c_{1'}(t)\right)&=h_1(t)\left[c_1(t)-c_{1'}(t)\right]\\ g_2\left(c_{2'}(t),c_2(t)\right)&=h_2(t)\left[c_{2'}(t)-c_2(t)\right]\end{aligned} \tag{44}$$

where $h_1(t)$ and $h_2(t)$ are the corresponding mass transfer coefficients, respectively. From $\mu_i=\mu_{0i}+RT\ln(c_i)(i=1,1',2',2)$, $c_i=\exp\left(\dfrac{\mu_i-\mu_{0i}}{RT}\right)$ is obtained. Substituting it into eq. (44) yields

$$\begin{aligned}g_1\left(\mu_1,\mu_{1'}\right)&=h_1(t)\exp\left(-\frac{\mu_{01}}{RT}\right)\left[\exp\left(\frac{\mu_1}{RT}\right)-\exp\left(\frac{\mu_{1'}}{RT}\right)\right]\\ g_2\left(\mu_{2'},\mu_2\right)&=h_2(t)\exp\left(-\frac{\mu_{02}}{RT}\right)\left[\exp\left(\frac{\mu_{2'}}{RT}\right)-\exp\left(\frac{\mu_2}{RT}\right)\right]\end{aligned} \tag{45}$$

Eq. (45) shows that the linear mass transfer law $g\propto\Delta(c)$ is equivalent to the common diffusive mass transfer law $\left[g\propto\Delta\left(\dfrac{\mu}{RT}\right)\right]$ [21, 24–30, 32, 43–52]. They are different mathematical representations for the same mass transfer manner. However, the mass transfer law $g\propto\Delta(c)$ expressed as a function of concentration is more convenient for calculation and analysis. It is assumed that at $t=0$ the working substance is in contact with high-chemical-potential reservoir and is separated from the low-chemical-potential reservoir by an instantaneous constant mass-flux branch. At a later time $t_1(0<t_1<\tau)$, the contact with the high-chemical -potential reservoir is broken and the working substance is placed in contact with the low-chemical-potential reservoir. Therefore, one has the following relationships:

$$h_1(t)=\begin{cases}h_1, & 0\leqslant t\leqslant t_1\\ 0, & t_1\leqslant t\leqslant\tau\end{cases},\quad h_2(t)=\begin{cases}0, & 0\leqslant t\leqslant t_1\\ h_2, & t_1\leqslant t\leqslant\tau\end{cases} \tag{46}$$

where h_1 and h_2 are constants, and t_1 is the time spent on the mass-absorbing process. Substituting eq. (44) into eq. (23) yields:

$$c_1=c_{1'}+\sqrt{C_cc_{1'}} \tag{47}$$

where $C_c = -\lambda_1/(h_1RT)$ is a constant to be determined. Eq. (47) further gives

$$c_{1'} = c_1 + C_c/2 - \sqrt{C_c c_1 + C_c^2/4} \tag{48}$$

Substituting eq. (48) into eq. (11) yields:

$$\dot{c}_1 = -\frac{h_1\left(1-c_1\right)^2\left(\sqrt{C_c c_1 + C_c^2/4} - C_c/2\right)}{G_{10}\left(1-c_{10}\right)},\quad c_1(0) = c_{10} \tag{49}$$

Eq. (49) determines the optimal concentration ($c_1^*(C_c,t)$) of the key component B_1 in the high-chemical -potential reservoir versus time. When the chemical engine is in contact with the high-chemical-potential reservoir, the optimal concentration ($c_{1'}^*(C_c,t)$) of the key component B_1 in the working substance of the chemical engine versus time is obtained by substituting $c_1^*(C_c,t)$ into eq. (48). Substituting eq. (44) into eq. (26) yields:

$$c_{2'} = \text{const} \tag{50}$$

Eq. (50) shows that the concentration of the key component B_2 in the working substance of the chemical engine is a constant when the chemical engine is in contact with the low-chemical-potential reservoir. Substituting $c_1^*(C_c,t)$ and $c_{1'}^*(C_c,t)$ into eq. (44) yields:

$$g_1\left(C_c,t\right) = h_1\left[c_1^*\left(C_c,t\right) - c_{1'}^*\left(C_c,t\right)\right] \tag{51}$$

The mass $N_1(C_c,t_1)$ that the chemical engine absorbs from the high-chemical-potential reservoir is obtained by substituting eq. (51) into eq. (1). The law of mass conservation gives $N_1 = N_2$. When the working substance of the chemical engine is in contact with the infinite potential capacity low-chemical-potential reservoir, the concentration of the key component B_2 in it is given by

$$c_{2'}^*\left(C_c,t_1\right) = c_2 + N_1\left(C_c,t_1\right)\Big/\left[h_2\left(\tau - t_1\right)\right] \tag{52}$$

Substituting $c_1^*(C_c,t)$, $c_{1'}^*(C_c,t)$ and $c_{2'}^*(C_c,t_1)$ into eq. (22), respectively, yields

$$\mu_i^*\left(C_c,t\right) = \mu_{01}\left(P,T\right) + RT\ln\left[c_i^*\left(C_c,t\right)\right],\quad i = 1,\ 1' \tag{53}$$

$$\mu_{2'}^*\left(C_c,t_1\right) = \mu_{02}\left(P,T\right) + RT\ln\left[c_{2'}^*\left(C_c,t_1\right)\right] \tag{54}$$

Substituting eqs. (51)–(54) into eq. (6) yields

$$\begin{aligned} W = {} & \int_0^{t_1}\Big\{h_1\left[c_1^*\left(C_c,t\right) - c_{1'}^*\left(C_c,t\right)\right]\mu_i^*\left(C_c,t\right)\Big\}\mathrm{d}t \\ & - N_1\left(C_c,t_1\right)\mu_{2'}^*\left(C_c,t_1\right) \end{aligned} \tag{55}$$

Eq. (55) determines the work output (W) per cycle for the optimal cycle configuration as a function of the parameter C_c and the time t_1. The optimal cycle configuration of the isothermal endoreversible chemical engine with a finite potential capacity high-chemical-potential reservoir and the mass transfer law $g \propto \Delta c$ for maximum work output is an isothermal endoreversible chemical engine cycle in which the concentration of the key component in the working substance at the low-chemical-potential side is a constant, while the concentrations of the key component in both the high-chemical-potential reservoir and the corresponding side working substance change nonlinearly with time (as shown in eq. (49)), and the relationship between them follows eq. (47). This is significantly different from that obtained with the mass transfer law $g \propto \Delta\mu$. From the above analysis, it is concluded that mass transfer laws have significant effects on the optimal cycle configurations of isothermal endoreversible chemical engines with finite potential capacity chemical potential reservoirs for maximum work output.

4.4 The case with the mass transfer law $g \propto \Delta c$ and an infinite potential capacity high-chemical-potential reservoir

The initial mass is $G_{10} \to \infty$ when the high-chemical-potential reservoir is an infinite potential capacity chemical potential reservoir. The concentration ($c_1(t)$) of the key component B_1 in the high-chemical-potential reservoir is equal to its initial concentration c_{10} from eq. (11). The chemical potential μ_1 is a constant because the equation $\mu_1 = \mu_{01} + RT\ln c_1$ holds. The chemical potential ($\mu_{1'}$) of the key component B_1 in the working substance of the chemical engine is also a constant from eq. (26). Now, the optimal cycle configuration consists of two constant chemical potential branches and two instantaneous constant mass-flux branches, which is analogous to the CA cycle [11] for the heat engine. As a result, when the high-chemical-potential reservoir is also an infinite potential capacity chemical potential reservoir, the optimal cycle configuration of the isothermal endoreversible chemical engine for maximum work output consists of two constant chemical potential branches and two instantaneous constant mass-flux branches, which is independent of the mass transfer law. The amounts of mass transfer along the constant chemical potential branches corresponding to the high- and low-chemical-potential sides are given by

$$N_1 = h_1\left(c_1 - c_{1'}\right)t_1,\quad N_2 = h_1\left(c_{2'} - c_2\right)\left(\tau - t_1\right) \tag{56}$$

respectively. The law of mass conservation gives $N_1 = N_2 = N$. Then the corresponding average power output $\overline{P}$ and the second law efficiency η are, respectively, given by

$$\overline{P} = W/\tau = \left(\mu_{1'} - \mu_{2'}\right)N/\tau \tag{57}$$

$$\eta = \frac{W}{W_{rev}} = \frac{\left(\mu_{1'} - \mu_{2'}\right)N}{\left(\mu_1 - \mu_2\right)N} = \frac{\mu_{1'} - \mu_{2'}}{\mu_1 - \mu_2} \tag{58}$$

From eqs. (56) and (58), one can obtain

$$c_{1'} = c_1 - N\big/\left(h_1t_1\right) \tag{59}$$

$$c_{2'} = c_2 + N\big/\left[h_2\left(\tau - t_1\right)\right] \tag{60}$$

$$\mu_{1'} - \mu_{2'} = \eta\left(\mu_1 - \mu_2\right) \tag{61}$$

Combining eqs. (59)–(61) yields

$$N=\frac{c_1-c_2\exp\left[(\eta-1)(\mu_{01}-\mu_{02})/(RT)+\eta\ln(c_1/c_2)\right]}{(h_1t_1)^{-1}+\left[h_2(\tau-t_1)\right]^{-1}\exp\left[(\eta-1)(\mu_{01}-\mu_{02})/(RT)+\eta\ln(c_1/c_2)\right]} \tag{62}$$

Substituting eqs. (61) and (62) into eq. (57) yields

$$\overline{P}=\frac{\eta\left[\mu_{01}-\mu_{02}+RT\ln(c_1/c_2)\right]\left\{c_1-c_2\exp\left[(\eta-1)(\mu_{01}-\mu_{02})/(RT)+\eta\ln(c_1/c_2)\right]\right\}}{\tau\left\{(h_1t_1)^{-1}+\left[h_2(\tau-t_1)\right]^{-1}\exp\left[(\eta-1)(\mu_{01}-\mu_{02})/(RT)+\eta\ln(c_1/c_2)\right]\right\}} \tag{63}$$

The optimal value of t_1 and the optimal power versus efficiency can be obtained from the extreme condition $\partial\overline{P}/\partial t_1=0$ as follows.

$$t_1=\tau\Big/\left\{1+\left\{h_1\exp\left[(\eta-1)(\mu_{01}-\mu_{02})/(RT)+\eta\ln(c_1/c_2)\right]/h_2\right\}^{0.5}\right\} \tag{64}$$

$$\overline{P}=\frac{h_1\eta\left[\mu_{01}-\mu_{02}+RT\ln(c_1/c_2)\right]\left\{c_1-c_2\exp\left[(\eta-1)(\mu_{01}-\mu_{02})/(RT)+\eta\ln(c_1/c_2)\right]\right\}}{\tau\left\{1+\sqrt{(h_1/h_2)\exp\left[(\eta-1)(\mu_{01}-\mu_{02})/(RT)+\eta\ln(c_1/c_2)\right]}\right\}^2} \tag{65}$$

Eq. (65) shows that the optimal power versus efficiency for the isothermal endoreversible chemical engine operating between two infinite potential capacity chemical potential reservoirs is a parabolic-like curve, which is analogous to that for the endoreversible heat engine operating between two infinite thermal capacity heat reservoirs [1–5, 11]. From eq. (65), one can obtain $\overline{P}=0$ when $\eta=\eta_{\min}=0$ and $\eta=\eta_{\max}=1$, and the power $\overline{P}$ achieves its maximum value during the point among the range $[0,1]$ of the efficiency η.

5 Conclusions

An isothermal endoreversible chemical engine operating between finite potential capacity high-chemical-potential reservoirs and infinite potential capacity low-chemical-potential reservoirs, in which the mass transfers between the working substance and the reservoirs obey a universal mass transfer law, was studied in this paper. Optimal control theory was applied to determine the optimal cycle configurations for maximum work output under the condition of the fixed total cycle time. The optimal cycle configuration with the mass transfer law $g\propto\Delta\mu$ is an isothermal endoreversible chemical engine cycle in which the chemical potential (or the concentration) of the key component in the working substance of low-chemical-potential side is a constant, while the chemical potentials (or the concentrations) of the key components in both the finite potential capacity high-chemical-potential reservoir and the corresponding side working substance change nonlinearly with time, and the difference of the chemical potentials (or the ratio of the concentrations) of the key component between the high-chemical-potential reservoir and the working substance is a constant. The optimal cycle configuration with the mass transfer law $g\propto\Delta c$ is different from that with the mass transfer law $g\propto\Delta\mu$ significantly. However, when the high-chemical-potential reservoir is also an infinite potential capacity reservoir, the optimal cycle configuration of the isothermal endoreversible chemical engine for maximum work output consists of two constant chemical potential branches and two instantaneous constant mass-flux branches (analogous to the CA cycle [11] of the heat engine), which is independent of the mass transfer law. The subject studied in this paper is a class of isothermal endoreversible chemical engines with finite potential capacity chemical potential reservoirs, which is more general than the common isothermal chemical engines with infinite potential capacity chemical potential reservoirs [19–32]. The idea and method used in this paper could be extended to research on optimizing performances of two-mass-reservoir chemical pump [43–45], three-mass-reservoir chemical pump [46], three-mass-reservoir chemical transformer [47, 48], four-mass-reservoir chemical pump [49, 50] and four-mass-reservoir chemical transformer [51, 52]. The results herein can provide some guidelines for optimal design and operation of real chemical engines, such as mass exchangers, electrochemical, photochemical and solid state devices.

The authors thank the two reviewers for their careful, unbiased and constructive suggestions, which led to this revised manuscript. This work was supported by the Program for New Century Excellent Talents of China (NCET-04-1006) and the Foundation for the Author of National Excellent Doctoral Dissertation of China (200136).

1 Andresen B, Berry RS, Ondrechen MJ, Salamon P. Thermodynamics for processes in finite time. *Acc Chem Res*, 1984, 17: 266–271

2 Berry RS, Kazakov VA, Sieniutycz S, Szwast Z, Tsirlin AM. *Thermodynamic Optimization of Finite Time Processes*. Chichester: Wiley, 1999

3 Chen L, Wu C, Sun F. Finite time thermodynamic optimization or entropy generation minimization of energy systems. *J Non-Equilib Thermodyn*, 1999, 24: 327–359

4 Chen L, Sun F. *Advances in Finite Time Thermodynamics: Analysis and optimization*. New York: Nova Science Publishers, 2004

5 Chen L. *Finite Time Thermodynamic Analysis of Irreversible Progresses and Cycles* (in Chinese). Beijing: High Education Press, 2005

6 Wang J, He J, Mao Z. Performance of quantum heat engine cycle with harmonic system. *Sci China Ser G-Phys Mech Astron*, 2007, 50: 163–176

7 Song H, Chen L, Sun F. Optimal configuration of a class of endoreversible heat engines for maximum efficiency with radiative heat transfer law. *Sci China Ser G-Phys Mech Astron*, 2008, 51: 1272–1286

8 Xia S, Chen L, Sun F. The optimal path of piston motion for Otto cycle with linear phenomenological heat transfer law. *Sci China Ser G-Phys Mech Astron*, 2009, 52: 708–719

9 Shu L, Chen L, Sun F. The minimal average heat consumption for heat-driven binary separation process with linear phenomenological heat transfer law. *Sci China Ser B-Chem*, 2009, 52: 1154–1163

10 Ma K, Chen L, Sun F. Optimal paths for a light-driven engine with linear phenomenological heat transfer law. *Sci China Chem*, 2010, 53(4): 917–926

11 Curzon FL, Ahlborn B. Efficiency of a Carnot engine at maximum power output. *Am J Phys*, 1975, 43: 22–24

12 Cutowicz-Krusin D, Procaccia J, Ross J. On the efficiency of rate process: Power and efficiency of heat engines. *J Chem Phys*, 1978, 69: 3898–3906

13 Ondrechen MJ, Andresen B, Mozurkewich M, Berry RS. Maximum work from a finite reservoir by sequential Carnot cycles. *Am J Phys*, 1981, 49: 681-685

14 Ondrechen MJ, Rubin MH, Band YB. The generalized Carnot cycles: a working fluid operating in finite time between heat sources and sinks. *J Chem Phys*, 1983, 78: 4721–4727

15 Amelkin SA, Andresen B, Burzler JM, Hoffmann KH, Tsirlin AM. Maximum power process for multi-source endoreversible heat engines. *J Phys D: Appl Phys*, 2004, 37: 1400–1404

16 Amelkin SA, Andresen B, Burzler JM, Hoffmann KH, Tsirlin AM. Thermo-mechanical systems with several heat reservoirs: maximum power processes. *J Non-Equlib Thermodyn*, 2005, 30: 67–80

17 Sieniutycz S. Spakovsky M. Finite time generalization of thermal exergy. *Energy Convers Mgmt*, 1998, 39:1423–1447

18 Sieniutycz S. Nonlinear thermokinetics of maximum work in finite time. *Int J Engng Sci*, 1998, 36: 577–597

19 de Vos A. *Endoreversible Thermodynamics of Solar Energy Conversion*. Oxford: Oxford University, 1992

20 de Vos A. Is a solar cell an endoreversible engine? *Solar Cells*, 1991, 31: 181–196

21 de Vos A. Endoreversible thermodynamics and chemical reactions. *J Phys Chem*, 1991, 95: 4534–4540

22 de Vos A. Entropy flaxes, endoreversibility and solar energy conversion. *J Appl Phys*, 1993, 74: 3631–3637

23 Tsirlin AM, Kazakov V, Kan NM, Trushkov VV. Thermodynamic analysis and thermodynamic efficiency of chemical reactors. *J Phys Chem B*, 2006, 110: 2338–2342

24 Gordon JM. Maximum work from isothermal chemical engines. *J Appl Phys*, 1993, 73: 8–11

25 Gordon JM, Orlov VN. Performance characteristics of endoreversible chemical engines. *J Appl Phys*, 1993, 74: 5303–5308

26 Chen L, Sun F, Wu C. Performance characteristics of isothermal chemical engines. *Energy Convers Mgmt*, 1997, 38: 1841–1846

27 Chen L, Sun F, Wu C. *Performance of chemical engines with a mass leak*. J Phys D: Appl Phys, 1998, 31: 1595–1600

28 Chen L, Sun F, Wu C, Gong J. Maximum power of a combined cycle isothermal chemical engine. *Appl Thermal Engng*, 1997, 17: 629–637

29 Chen L, Duan H, Sun F, Wu C. Performance of a combined-cycle chemical engine with mass leak. *J Non-Equibri Thermodyn*, 1999, 24: 280–290

30 Lin G, Chen J, Bruck E. Irreversible chemical-engines and their optimal performance analysis. *Appl Energy*, 2004, 78: 123–136

31 Tsirlin AM, Leskov EE, Kazakov V. Finite time thermodynamics: limiting performance of diffusion engines and membrane systems. *J. Phys Chem A*, 2005, 109: 9997–10003

32 Chen L, Xia D, Sun F. Optimal performance of an endoreversible chemical engine with diffusive mass transfer law. Proc IMechE, Part C: J Mech. *Engng Sci*, 2008, 222: 1535–1539

33 Sieniutycz S. Analysis of power and entropy generation in a chemical engine. *Int J Heat Mass Transfer*, 2008, 51: 5859–5871

34 Sieniutycz S. Thermodynamics of chemical power generators. *Chem Process Engng*, 2008, 29: 321–335

35 Sieniutycz S. Complex chemical systems with power production driven by heat and mass transfer. *Int J Heat Mass Transfer*, 2009, 52: 2453–2465

36 Xia S, Chen L, Sun F. Maximum power configuration for multi-reservoir chemical engines. *J Appl Phys*, 2009, 105: 114905

37 Yan Z, Chen J. Optimal performance of a generalized Carnot cycle for another linear heat transfer law. *J Chem Phys*, 1990, 92: 1994–1998

38 Chen L, Sun F, Wu C. Optimal configuration of a two-heat-reservoir heat-engine with heat leak and finite thermal capacity. *Appl Energy*, 2006, 83: 71–81

39 Xiong G, Chen J, Yan Z. The effect of heat transfer law on the performance of a generalized Carnot cycle (in Chinese). *J Xiamen University (Nature Science)*, 1989, 28: 489–494

40 Chen L, Zhu X, Sun F, Wu C. Optimal configurations and performance for a generalized Carnot cycle assuming the heat transfer law $Q \propto (\Delta T)^m$. *Appl Energy*, 2004, 78: 305–313

41 Chen L, Zhu X, Sun F, Wu Chih. Effect of mixed heat resistance on the optimal configuration and performance of a heat-engine cycle. *Appl Energy*, 2006, 83: 537–544

42 Li J, Chen L, Sun F. Optimal configuration for a finite high-temperature source heat engine cycle with complex heat transfer law. *Sci China Ser G-Phys Mech Astron*, 2009, 52: 587–592

43 Lin G, Chen J. Optimal analysis on the cyclic performance of a class of chemical pumps. *Appl Energy*, 2001, 70: 35–47

44 Lin G, Chen J, Brück E, Hua B. Optimization of performance characteristics in a class of irreversible chemical pumps. *Math Compu Modell*, 2006, 43: 743–753

45 Xia D, Chen L, Sun F. Optimal performance of a chemical pump with diffusive mass transfer law. *Int J Sustainable Energy*, 2008, 27: 39–47

46 Lin G, Chen J, Hua B. General performance characteristics of an irreversible three source chemical pump. *Energy Convers Mgmt*, 2003, 44: 1719–1731

47 Lin G, Chen J, Wu C. The equivalent combined cycle of an irreversible chemical potential transformer and its optimal performance. *Exergy, An Int J*, 2002, 2: 119–124

48 Xia D, Chen L, Sun F, Wu C. Optimal performance of an endoreversible three-mass-reservoir chemical potential transformer with diffusive mass transfer law. *Int J Ambient Energy*, 2008, 29: 9–16

49 Xia D, Chen L, Sun F, Wu C. Endoreversible four-mass-reservoir chemical pump. *Appl Energy*, 2007, 84: 56–65

50 Chen L, Xia D, Sun F. Fundamental optimal relation of a generalized irreversible four-reservoir chemical pump. *Proc IMechE*, Part C: J Mech Engng Sci, 2008, 222: 1523–1534

51 Xia D, Chen L, Sun F. Performance of a four-reservoir chemical potential transformer with irreversible mass transfer and mass leakage. *Appl Thermal Engng*, 2007, 27: 1534–1542

52 Xia D, Chen L, Sun F. Optimal performance of a generalized irreversible four-reservoir isothermal chemical potential transformer. *Sci China Ser B-Chem*, 2008, 51: 958–970