Optimal configuration of a finite mass reservoir isothermal chemical engine for maximum work output with linear mass transfer law

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An isothermal endoreversible chemical engine operating between a finite high-chemical- potential reservoir and an infinite low-chemical-potential reservoir in which the mass transfer between the working fluid and the mass reservoirs obeys the linear mass-transfer law [$g \propto \Delta\mu$], is put forward in this paper. Optimal control theory is applied to determine the optimal cycle configuration corresponding to the maximum work output for the fixed total cycle time. The optimal cycle configuration is an isothermal endoreversible chemical engine cycle in which the chemical potential (concentration) of the key component in the finite high-chemical- potential mass reservoir and that in the working fluid change nonlinearly with time. The difference in chemical potentials (ratio of the concentrations) between the key component in the finite mass reservoir and the working fluid is a constant, and the chemical potential (concentration) of the key component in the working fluid at the low chemical potential side is also a constant. A numerical example is provided, and the effects of the concentration changes in the key component in the finite high-chemical-potential reservoir on the optimal configuration of the chemical engine are analyzed. The obtained results are compared with those obtained for an endoreversible heat engine operating between a finite heat source and an infinite heat sink with Newton's heat transfer law [$q \propto \Delta T$] in the heat transfer processes. The object studied in this paper is general, and the results could provide some guidelines for the optimal design and operation of real chemical engines.

Keywords: Finite high-chemical-potential reservoir; isothermal endoreversible chemical engine; maximum work output; optimal control; generalized thermodynamic optimization.

En el presente trabajo se presenta un motor químico endoreversible isotérmico trabajando entre un recipiente finito de alto potencial químico y un recipiente infinito de bajo potencial químico, en el cual, la transferencia de masa entre el fluido de trabajo y la masa contenida obedece a la ley lineal de transferencia de masa [$g \propto \Delta\mu$]. Se aplica la teoría del control óptimo para determinar la configuración óptima del ciclo, correspondiente al máximo trabajo de salida para el tiempo total del ciclo. La configuración del ciclo óptimo es el de un motor químico endoreversible isotérmico en el cual, el potencial químico (concentración) de la componente clave en el recipiente finito masivo de alto potencial químico y el del fluido de trabajo cambian de forma no lineal con el tiempo. La diferencia en los potenciales químicos (cociente de las concentraciones) entre el componente clave del recipiente finito masivo y el fluido de trabajo es una constante, y el potencial químico (concentración) del componente clave en el fluido de trabajo del lado del potencial químico bajo es también una constante. Se proporciona un ejemplo numérico donde se analizan los efectos del cambio en la concentración en la componente clave del recipiente finito con alto potencial químico respecto de la configuración óptima del motor químico. Los resultados obtenidos se comparan con los obtenidos para un motor térmico endoreversible que trabaja entre una fuente de calor finita y un disipador de calor infinito, que obedece a la ley de Newton de transferencia de calor ($q \propto \Delta T$) en los procesos de tranferencia de calor. El objeto de estudio en el presente trabajo es general y los resultados podrían proporcionar algunas pautas para el diseño óptimo y funcionamiento de motores químicos reales.

Descriptores: Recipiente finito de alto potencial químico; motor químico isotérmico endoreversible; máximo trabajo de salida; control óptimo; optimización termodinámica generalizada.

1. Introduction

Determining the optimal thermodynamic process for the given optimization objectives is one of the standard problems in finite-time thermodynamics [1-17]. Curzon and Ahlborn [18] showed that the efficiency of an endoreversible heat engine with Newton's heat transfer law [$q \propto \Delta T$] at maximum power point is $\eta_{CA} = 1 - \sqrt{T_L/T_H}$. Cutowicz-Krusin *et al.* [19] proved that, in all acceptable cycles, an endoreversible Carnot cycle with larger compression ratio can produce maximum power, *i.e.* the Curzon-Ahlborn cycle [18] is the optimal configuration with only First and Second Law constraints. Ondrechen *et al.* first investigated the problem of maximizing work output from a finite reservoir by sequential Carnot cycles [20], and further investigated the optimal configuration of an endoreversible heat engine with finite heat reservoirs and Newton's heat transfer law [21].

Amelkin *et al.* [22,23] investigated the optimal configuration of a multi-heat-reservoir heat engine with stationary temperature reservoirs for maximum power output. Sieniutycz and von Sparkovsky [24] obtained the extremal work and optimal temperature profile of multistage endoreversible continuous heat engine systems with one reservoir of finite thermal capacity. Sieniutycz [25] further obtained those of multistage endoreversible discrete heat engine systems with one reservoir of finite thermal capacity.

The idea and method of finite time thermodynamic optimization for heat engines can be extended to generalized thermodynamic processes and devices. De Vos [26-29] has extended the definition of the endoreversible heat engine to a generalized endoreversible engine by generalizing heat reservoirs to heat and mass reservoirs and heat exchangers to heat and mass exchangers. Gordon [30] investigated the problem

of maximizing work output from a finite chemical potential reservoir by sequential isothermal chemical engines. Gordon and Orlov [31] further investigated the optimal configuration of an isothermal endoreversible chemical engine operating between two infinite chemical-potential reservoirs for maximizing power output. The optimal cycle configuration of endoreversible chemical engine with finite reservoirs was also discussed qualitatively in Ref. 31. Chen *et al*. [32-34] derived the optimal relation between the power output and the second law efficiency of the isothermal endoreversible chemical engine and the combined-cycle isothermal endoreversible chemical engines with the sole irreversibility of mass transfer, and analyzed the effect of mass leakage on the performance of isothermal chemical engines [35]. Lin *et al*. [36] 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*. [37] derived the minimum entropy generation rate and the maximum power output of a class of isothermal endoreversible chemical engines. Tsirlin *et al*. [38] also analyzed the performance of chemical reactors. Chen *et al*. [39] further investigated the optimal performance of an endoreversible chemical engine with the diffusive mass transfer law. Sieniutycz [40-42] investigated the optimal performance of multistage endoreversible continuous chemical engine systems with simultaneous heat and mass transfer by applying Hamilton-Jacobi-Bellman equations. Xia *et al*. [43] derived the optimal cycle configuration of the multi-reservoir isothermal endoreversible chemical engine for maximum work output per cycle. Previous works have been focusing on investigating the optimal performance [26-28,30,33-36,38-43] and optimal configuration [29,37] of an isothermal chemical engine operating between infinite reservoirs. The optimal cycle configuration of endoreversible chemical engine with finite reservoirs was also discussed qualitatively in Ref. 31, but the model of finite mass reservoir was not described in detail and the results obtained in Ref. 31 did not reflect the essence of optimal cycle configuration of the isothermal endoreversible chemical engine with finite mass reservoirs.

Linetskii and Tsirlin [44], and Andresen and Gordon [45] investigated the optimal configuration of heat transfer processes in heat exchangers with Newton's heat transfer law for minimizing entropy generation. Chen *et al*. [46] investigated the optimal configuration of heat transfer processes in heat exchangers with a universal heat transfer law for minimizing entropy generation. Based on the analogy between heat transfer and mass transfer, Tsirlin [47] and Tsirlin*et al*. [48,49] derived the optimal configuration of finite rate mass transfer processes in mass exchangers for minimizing entropy generation by using optimal control theory. On the basis of research into the optimal configuration of heat engines for maximum power output [21], and with the method of analogy and transplanting, this paper will establish a model of an isothermal endoreversible chemical engine operating between a finite

high-chemical-potential mass reservoir and an infinite low-chemical-potential mass reservoir in which the mass transfer between the working fluid of the chemical engine and mass reservoirs obeys the linear mass-transfer law [$g \propto \Delta\mu$]. The optimal cycle configuration of the isothermal endoreversible chemical engine for maximum work output will be derived for the fixed total cycle time by using optimal control theory.

2. Isothermal chemical engine model

The isothermal endoreversible chemical engine to be considered in this paper is shown in Fig. 1. It operates between a finite high-chemical-potential mass reservoir and an infinite low- chemical-potential reservoir. The total mass of the material in the high-chemical-potential reservoir is given by $G_1(t)$, and its initial mass is given by $G_1(0) = G_{10}$. The high-chemical- potential reservoir is finite in size, so the chemical potential of the key component B_1 in it will change with the mass transfer between the high-chemical-potential reservoir and the working fluid of the chemical engine. Let the concentration (mole fraction) and the chemical potential of the key component B_1 in the high-chemical-potential reservoir be $c_1(t)$ and $\mu_1(c_1)$, respectively. The chemical reaction in the chemical engine is assumed to be a single isomerization reaction $B_1 \Leftrightarrow B_2$ [40-42]. The heat absorbed or released due to the chemical reaction is very small and can be neglected, so the temperature over the cycle time is a
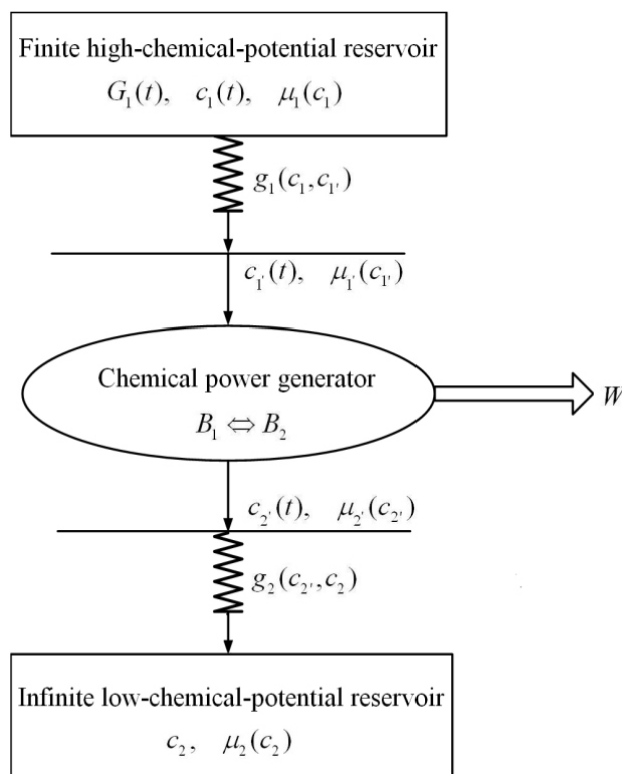

FIGURE 1. Model of the isothermal endoreversible chemical engine.

constant. The concentration and the chemical potential of the key component B_1 in the working fluid of chemical engine on 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 corresponding to the low-chemical-potential side are given by $c_{2'}(t)$ and $\mu_{2'}(c_{2'})$, respectively. The low-chemical-potential reservoir is assumed, for simplicity, to be infinite in size and therefore 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. It is assumed that the mass exchanges between the mass reservoirs and the working fluid of the chemical engine obey the mass transfer law of linear irreversible thermodynamics $[g \propto \Delta\mu]$. Then:

$$N_1 = \int_0^\tau g_1(c_1(t), c_{1'}(t))dt$$

$$= \int_0^\tau h_1(t)[\mu_1(c_1) - \mu_{1'}(c_{1'})]dt \qquad (1)$$

$$N_2 = \int_0^\tau g_2(c_{2'}(t), c_2(t))dt$$

$$= \int_0^\tau h_2(t)[\mu_{2'}(c_{2'}) - \mu_2(c_2)]dt \qquad (2)$$

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 the low-chemical-potential sides, respectively, and $h_1(t)$ and $h_2(t)$ are the corresponding mass- transfer coefficients, respectively. It is assumed that at $t = 0$ the working fluid is in contact with the 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 fluid is placed in contact with the low-chemical-potential reservoir. Therefore, one has the following relationships:

$$h_1(t) = \begin{cases} h_1, & 0 \le t \le t_1 \\ 0, & t_1 \le t \le \tau \end{cases} \qquad (3)$$

$$h_2(t) = \begin{cases} 0, & 0 \le t \le t_1 \\ h_2, & t_1 \le t \le \tau \end{cases} \qquad (4)$$

where h_1 and h_2 are constants. The law of mass conservations gives $N_1 = N_2$, *i.e.*

$$\int_0^\tau h_1(t)[\mu_1(c_1) - \mu_{1'}(c_{1'})]dt$$

$$- \int_0^\tau h_2(t)[\mu_{2'}(c_{2'}) - \mu_2(c_2)]dt = 0. \qquad (5)$$

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

$$\int_0^\tau [U_1(t) - U_2(t)]dt - \int_0^\tau P(t)dt = 0, \qquad (6)$$

where $U_1(t)$ and $U_2(t)$ are the total energy flow rates between the two chemical potential reservoirs and the working fluid of the chemical engine, respectively, and $P(t)$ is the power output of the chemical engine. In terms of the second law of thermodynamics, the entropy change of the working fluid of the isothermal endoreversible chemical engine for the whole cycle is zero, *i.e.* the entropy flux input is equal to the entropy flux output:

$$\left\{ \int_0^\tau [U_1(t) - g_1(c_1, c_{1'})\mu_{1'}(c_{1'})]dt \right.$$

$$\left. - \int_0^\tau [U_2(t) - g_2(c_{2'}, c_2)\mu_{2'}(c_{2'})]dt \right\}/T = 0, \qquad (7)$$

where T is the temperature during the mass transfer process, which is a constant. Using Eqs. (6) and (7), the work output per cycle W is

$$W = \int_0^\tau P(t)dt$$

$$= \int_0^\tau [g_1(c_1, c_{1'})\mu_{1'}(c_{1'}) - g_2(c_{2'}, c_2)\mu_{2'}(c_{2'})]dt. \qquad (8)$$

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

$$\frac{dG_1}{dt} = -g_1(c_1, c_{1'}), G_1(0) = G_{10}. \qquad (9)$$

Consider that there is a transfer of the key component B_1 only between the high-chemical- potential reservoir and the working fluid of the chemical engine; then

$$\frac{d(G_1 c_1)}{dt} = \frac{dG_1}{dt}. \qquad (10)$$

From Eqs. (9) and (10), it follows that:

$$\frac{dc_1}{dt} = -\frac{(1 - c_1)}{G_1} g(c_1, c_{1'}). \qquad (11)$$

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

$$G_1(1 - c_1) = \tilde{G}, \qquad (12)$$

where $\widehat{G} = G_{10}(1 - c_{10})$ is a constant. Substituting Eq. (12) into Eq. (11) yields:

$$\dot{c}_1 = -\frac{(1 - c_1)^2}{\widehat{G}} g(c_1, c_{1'}), \qquad (13)$$

where $\dot{c}_1 = dc_1/dt$.

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. (8) subjected to the constraints of Eqs. (5) and (13). Apparently, it is a typical optimal control problem. Correspondingly, the modified Lagrangian L is given by

$$L = g_1(c_1, c_{1'})\mu_{1'}(c_{1'}) - g_2(c_{2'}, c_2)\mu_{2'}(c_{2'})$$
$$+ \lambda\{g_1(c_1, c_{1'}) - g_2(c_{2'}, c_2)\}$$
$$+ u(t)\left\{\dot{c}_1 + \frac{(1 - c_1)^2}{\widehat{G}} g_1(c_1, c_{1'})\right\}, \qquad (14)$$

where λ is the Lagrangian constant and $u(t)$ is a function of time. The paths for the concentration of two key components in the working fluid which result in the maximum work for a given time interval $\{0, \tau\}$ may now be obtained from the solutions of the Euler–Lagrange equations. The Euler–Lagrange equations are given by

$$\frac{\partial L}{\partial c_1} - \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{c}_1}\right) = 0, \qquad \frac{\partial L}{\partial c_{1'}} - \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{c}_{1'}}\right) = 0,$$
$$\frac{\partial L}{\partial c_{2'}} - \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{c}_{2'}}\right) = 0. \qquad (15)$$

Substituting Eq. (14) into Eq. (15) yields

$$\frac{\partial g_1}{\partial c_1}\left(\mu_{1'} + \lambda + u(t)\frac{(1 - c_1)^2}{\widehat{G}}\right)$$
$$- 2u(t)g_1\frac{(1 - c_1)}{\widehat{G}} - \dot{u}(t) = 0, 0 \le t \le t_1 \qquad (16)$$

$$\frac{\partial g_1}{\partial c_{1'}}\left(\mu_{1'} + \lambda + u(t)\frac{(1 - c_1)^2}{\widehat{G}}\right)$$
$$+ g_1\frac{\partial \mu_{1'}}{\partial c_{1'}} = 0, \qquad 0 \le t \le t_1 \qquad (17)$$

$$\frac{\partial g_2}{\partial c_{2'}}(\mu_{2'} + \lambda) + g_2\frac{\partial \mu_{2'}}{\partial c_{2'}} = 0, \qquad t_1 \le t \le \tau \qquad (18)$$

$$\dot{u}(t) = 0, \qquad t_1 \le t \le \tau. \qquad (19)$$

Since $g_2 = h_2(\mu_{2'} - \mu_2)$, one obtains

$$(\partial g_2/\partial c_{2'})(\partial \mu_{2'}/\partial c_{2'}) = h_2,$$

from which Eq. (18) leads to

$$\mu_{2'} = \frac{\mu_2 - \lambda}{2}, \qquad t_1 \le t \le \tau, \qquad (20)$$

where both μ_2 and λ are constants. From Eq. (20), one can see that the chemical potential ($\mu_{2'}$) of the key component B_2 in the working fluid is also a constant when the chemical engine is in contact with the infinite low-chemical-potential reservoir. Since $g_1 = h_1(\mu_1 - \mu_{1'})$, one also obtains $(\partial g_1/\partial c_{1'})/(\partial \mu_{1'}/\partial c_{1'}) = -h_1$, from which Eq. (18) leads to

$$u(t) = \frac{\widehat{G}}{(1 - c_1)^2}(\mu_1 - 2\mu_{1'} - \lambda), \qquad 0 \le t \le t_1 \qquad (21)$$

Differentiating Eq. (21) with respect to time t yields:

$$\dot{u}(t) = \frac{2\widehat{G}\dot{c}_1}{(1 - c_1)^3}(\mu_1 - 2\mu_{1'} - \lambda)$$
$$+ \frac{\widehat{G}}{(1 - c_1)^2}(\dot{\mu}_1 - 2\dot{\mu}_{1'}), \qquad 0 \le t \le t_1. \qquad (22)$$

From Eq. (13), one can obtain

$$\frac{\widehat{G}}{(1 - c_1)^2} = -\frac{g(c_1, c_{1'})}{\dot{c}_1}. \qquad (23)$$

Substituting Eq. (23) into Eq. (22) yields:

$$\dot{u}(t) = -\frac{2\widehat{G}g_1(c_1, c_{1'})}{(1 - c_1)}(\mu_1 - 2\mu_{1'} - \lambda)$$
$$- \frac{g_1(c_1, c_{1'})}{\dot{c}_1}(\dot{\mu}_1 - 2\dot{\mu}_{1'}), \qquad 0 \le t \le t_1. \qquad (24)$$

Substituting Eqs. (21) and (24) into Eq. (16) yields:

$$\frac{\partial g_1}{\partial c_1}(\mu_1 - \mu_{1'}) + \frac{g(c_1, c_{1'})}{\dot{c}_1}(\dot{\mu}_1 - 2\dot{\mu}_{1'}) = 0,$$
$$0 \le t \le t_1. \qquad (25)$$

From $g_1 = h_1(u_1 - u_{1'})$, one can further obtain $\partial g_1/\partial c_1 = h_1\partial \mu_1/\partial c_1$. Substituting it into Eq. (25) yields:

$$\mu_1 - \mu_{1'} = const = C_\mu, \quad 0 \le t \le t_1, \qquad (26)$$

where C_μ is an integration constant. Eq. (26) shows that the difference between the chemical potential of the key component B_1 in the high-chemical-potential reservoir and that in the working fluid is a constant when the chemical engine is in contact with the high-chemical-potential reservoir.

Then the entropy generation (ΔS_1) due to the finite rate mass transfer between the high- chemical-potential reservoir and the working fluid of the chemical engine is given by

$$\Delta S_1 = \int_0^\tau \{g_1(c_1, c_{1'})[\mu_1(c_1) - \mu_{1'}(c_{1'})]\}dt/T$$

$$= h_1 C_\mu^2 t_1/T. \tag{27}$$

The entropy generation (ΔS_2) due to the finite rate mass transfer between the working fluid of the chemical engine and the low-chemical-potential reservoir is given by

$$\Delta S_2 = \int_0^\tau \{g_2(c_{2'}, c_2)[\mu_{2'}(c_{2'}) - \mu_2(c_2)]\}dt/T$$

$$= h_1^2 C_\mu^2 t_1^2/[h_2(\tau - t_1)T] \tag{28}$$

The total entropy generation per cycle ΔS is given by

$$\Delta S = \Delta S_1 + \Delta S_2$$

$$= h_1 C_\mu^2 t_1/T + h_1^2 C_\mu^2 t_1^2/[h_2(\tau - t_1)T] \tag{29}$$

According to Refs. 37, 47 to 49, the chemical potential (μ_i) of the i-th component in a mixture that is similar in properties to ideal gases or ideal solutions can be expressed as

$$\mu_i(c_i) = \mu_{0i}(P, T) + RT \ln c_i, \quad i = 1, \ 1', \ 2', \ 2, \tag{30}$$

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 $\mu_0(P, T)$ is the chemical potential of the pure i-th component (known for most of substances). Substituting Eq. (30) into Eqs. (1) and (2), respectively, yields:

$$c_1(t)/c_{1'}(t) = \exp(C_\mu/RT). \tag{31}$$

From Eq. (31), one can see that the ratio of the concentration of the key component B_1 in the high-chemical-potential reservoir to that in the working fluid of the chemical engine is a constant for the optimal cycle configuration. Substituting Eq. (30) into Eqs. (1) and (2), respectively, yields:

$$N_1 = \int_0^\tau g_1(c_1, c_{1'})dt = h_1 RT \ln(c_1/c_{1'})t_1$$

$$= h_1 C_\mu t_1 \tag{32}$$

$$N_2 = \int_0^\tau g_2(c_{2'}, c_2)dt = h_2 RT \ln(c_{2'}/c_2)(\tau - t_1). \tag{33}$$

Combining Eqs. (9) with (32), one can obtain the total mass ($G_1(t)$) of the material in the high-chemical-potential reservoir versus time, which is given by

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

Substituting Eq. (34) into Eq. (11) yields

$$\frac{dc_1}{dt} = -\frac{(1 - c_1)}{G_{10} - h_1 C_\mu t} h_1 C_\mu, \quad c_1(0) = c_{10}. \tag{35}$$

From Eq. (35), one can obtain the concentration ($c_1(t)$) of the key component B_1 in the high- chemical-potential reservoir versus time, which is given by

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

Substituting Eq. (36) into Eq. (31), one can obtain the concentration of the key component B_1 in the working fluid of the chemical engine versus time during the mass absorbed process, which is give by

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

Combining Eqs. (5), (32) with (33), one can get the concentration of the key component B_2 in the working fluid of the chemical engine during the mass released process, which is given by

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

From Eq. (8), one can further obtain the work output per cycle, which is given by

$$W = h_1 C_\mu \left[\int_0^{t_1} \mu_{1'} dt - t_1 (\int_{t_1}^\tau \mu_{2'} dt)/(\tau - t_1) \right]. \tag{39}$$

Combining Eqs. (30) and (37)-(39) yields

$$W = h_1 C_\mu \left\{ \int_0^{t_1} \{\mu_{01} - C_\mu + RT \ln[1 - G_{10}(1 - c_{10})/(G_{10} - h_1 C_\mu t)]\}dt - \mu_2 t_1 - h_1 C_\mu t_1^2/[h_2(\tau - t_1)] \right\}. \tag{40}$$

Equation (40) further gives

$$W = h_1 C_\mu RT \int\limits_0^{t_1} \left\{ \ln\left[1 - \frac{G_{10}(1-c_{10})}{G_{10} - h_1 C_\mu t}\right]\right\} dt - h_1 C_\mu^2 t_1 \frac{h_2(\tau - t_1) + h_1 t_1}{h_2(\tau - t_1)} + h_1 C_\mu t_1 (\Delta\mu_0 - RT \ln c_2) \qquad (41)$$

where $\Delta\mu_0 = \mu_{01} - \mu_{02}$. Integrating the first term of Eq. (41) yields

$$W = RT\left[h_1 C_\mu t_1 \ln\left(\frac{G_{10}c_{10} - h_1 C_\mu t_1}{G_{10} - h_1 C_\mu t_1}\right) + G_{10}\ln\left(\frac{G_{10} - h_1 C_\mu t_1}{G_{10}}\right) - G_{10}c_{10}\ln\left(\frac{G_{10}c_{10} - h_1 C_\mu t_1}{G_{10}c_{10}}\right)\right]$$

$$+ h_1 C_\mu t_1 (\Delta\mu_0 - RT \ln c_2) - h_1 C_\mu^2 t_1 \frac{h_2(\tau - t_1) + h_1 t_1}{h_2(\tau - t_1)}. \qquad (42)$$

The reversible work per cycle is given by

$$W_{rev} = h_1 C_\mu \left[\int\limits_0^{t_1} \mu_1 dt - t_1 (\int\limits_{t_1}^{\tau} \mu_2 dt)/(\tau - t_1)\right]. \qquad (43)$$

Combining Eqs. (30), (36) with (43) yields

$$W_{rev} = RT\left[h_1 C_\mu t_1 \ln\left(\frac{G_{10}c_{10} - h_1 C_\mu t_1}{G_{10} - h_1 C_\mu t_1}\right) + G_{10}\ln\left(\frac{G_{10} - h_1 C_\mu t_1}{G_{10}}\right) - G_{10}c_{10}\ln\left(\frac{G_{10}c_{10} - h_1 C_\mu t_1}{G_{10}c_{10}}\right)\right]$$

$$+ h_1 C_\mu t_1 (\Delta\mu_0 - RT \ln c_2). \qquad (44)$$

From Eqs. (29), (42) and (44), one can obtain

$$W = W_{rev} - T\Delta S. \qquad (45)$$

From Eq. (45), one can see that the work output per cycle of the isothermal endoreversible chemical engine with the finite high-chemical-potential reservoir is equal to the difference between the reversible work per cycle and the exergy lost. This result proves that the performance limits implied by the finite time thermodynamics are more realistic, stronger than those implied by classical thermodynamics. 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 could only be solved numerically.

When the high-chemical-potential reservoir is a finite mass reservoir, the initial mass G_{10} is also a finite value. From Eq. (36), the concentration ($c_1(t)$) of the key component B_1 in the high-chemical-potential reservoir changes non-linearly with time t. Because $\mu_1 = \mu_{01} + RT \ln c_1$, the chemical potential μ_1 also changes non-linearly with time t. From Eq. (26), one can see that the chemical potential ($\mu_{1'}$) of the key component B_1 in the working fluid of the chemical engine changes non-linearly with time t during the mass absorbed process also. Both μ_1 and $\mu_{1'}$ change non-linearly with time, but the difference between them is a constant, *i.e.* the mass transfer rate g_1 is a constant. The optimal cycle configuration of the isothermal endoreversible chemical engine operating between a finite high-chemical-potential and an infinite low-chemical-potential reservoir for maximum work output consists of two constant mass transfer rate branches and two instantaneous constant mass-flux branches. By defining

$$\mu_1^* = \frac{1}{t_1} \int\limits_0^t \mu_1(t)dt$$

and

$$\mu_{1'}^* = \frac{1}{t_1} \int\limits_0^t \mu_{1'}(t)dt,$$

the average power output ($\bar{P}$) per cycle and the second law efficiency η are

$$\bar{P} = W/\tau = (\mu_{1'}^* - \mu_{2'})N_1/\tau \qquad (46)$$

$$\eta = \frac{W}{W_{rev}} = \frac{(\mu_{1'}^* - \mu_{2'})N_1}{(\mu_1^* - \mu_2)N_1} = \frac{(\mu_{1'}^* - \mu_{2'})}{(\mu_1^* - \mu_2)}, \qquad (47)$$

respectively. From Eqs. (1), (2) and (47), one can obtain

$$\mu_{1'}^* = \mu_1^* - N_1/(h_1 t_1) \qquad (48)$$

$$\mu_{2'} = \mu_2 + N_1/[h_2(\tau - t_1)] \qquad (49)$$

$$(\mu_{1'}^* - \mu_{2'}) = \eta(\mu_1^* - \mu_2) \qquad (50)$$

Combining Eqs. (1), (2) and (47) yields

$$\bar{P} = \frac{\eta(1-\eta)(\mu_1^* - \mu_2)^2}{\tau\{(h_1 t_1)^{-1} + [h_2(\tau - t_1)]^{-1}\}} \qquad (51)$$

For the finite high-chemical-potential reservoir, μ_1^* is a function of time t_1. Comparing Eqs. (41) with (42), one obtains μ_1^*, which is given by

$$\mu_1^* = \mu_{01} + RT\left[\ln\left(\frac{G_{10}c_{10} - h_1 C_\mu t_1}{G_{10} - h_1 C_\mu t_1}\right)\right.$$
$$+ \frac{G_{10}}{h_1 C_\mu t_1}\ln\left(\frac{G_{10} - h_1 C_\mu t_1}{G_{10}}\right)$$
$$\left. - \frac{G_{10}c_{10}}{h_1 C_\mu t_1}\ln\left(\frac{G_{10}c_{10} - h_1 C_\mu t_1}{G_{10}c_{10}}\right)\right] \quad (52)$$

From Eq. (52), one can see that there is no closed-form solution for the extreme condition $\partial \bar{P}/\partial t_1 = 0$. However, from Eq. (51), one can see that there are two zero points for the average power output $\bar{P}$, *i.e.* $\bar{P} = 0$ when $\eta = \eta_{\min} = 0$ and $\eta = \eta_{\max} = 1$. The optimal relationship between the power output and the efficiency of the isothermal endoreversible chemical engine with the finite high-chemical-potential reservoir is a parabolic-like curve, which is analogous to that for the endoreversible heat engine with the finite heat source [21].

When the high-chemical-potential reservoir is an infinite mass reservoir, the initial mass $G_{10} \to \infty$. From Eq. (36), 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 $\mu_1 = \mu_{01} + RT\ln c_1$, one can see that the chemical potential μ_1 is a constant. From Eq. (26), one can also see that the chemical potential ($\mu_{1'}$) of the key component B_1 in the working fluid of the chemical engine is also a constant. The optimal cycle configuration of the isothermal endoreversible chemical engine operating between two infinite mass reservoirs for maximum work output consists of two constant chemical potential branches and two instantaneous constant mass-flux branches, which is analogous to the CA cycle for the endoreversible heat engine [18]. This is the same result as that obtained in Refs. 31 and 37. The corresponding average power output $\bar{P}$ and the second law efficiency η are

$$\bar{P} = W/\tau = (\mu_{1'} - \mu_{2'})N_1/\tau \quad (53)$$

$$\eta = \frac{W}{W_{rev}} = \frac{(\mu_{1'} - \mu_{2'})N_1}{(\mu_1 - \mu_2)N_1} = \frac{\mu_{1'} - \mu_{2'}}{\mu_1 - \mu_2}. \quad (54)$$

Combining Eqs. (1), (2), (46) with (47) yields

$$\bar{P} = \frac{\eta(1-\eta)(\mu_1 - \mu_2)^2}{\tau\{(h_1 t_1)^{-1} + [h_2(\tau - t_1)]^{-1}\}}. \quad (55)$$

From the extreme condition $\partial \bar{P}/\partial t_1 = 0$, one can obtain

$$t_1 = \frac{\tau}{[1 + (h_1/h_2)^{0.5}]}$$

and the optimal power versus efficiency, *i.e.*

$$\bar{P} = \frac{h_1 \eta(1-\eta)(\mu_1 - \mu_2)^2}{[1 + (h_1/h_2)^{0.5}]^2}. \quad (56)$$

This is the same result as that obtained in Ref. 32. Equation (56) shows that the optimal relationship between the power and the efficiency for the isothermal endoreversible chemical engine operating between two infinite mass reservoirs is a parabolic-like curve, which is analogous to that for the endoreversible heat engine operating between two infinite heat reservoirs [18]. From Eq. (56), one can see that $\bar{P} = 0$ when $\eta = \eta_{\min} = 0$ and $\eta = \eta_{\max} = 1$, and

$$\bar{P} = \bar{P}_{\max} = \frac{h_1(\mu_1 - \mu_2)^2}{4[1 + (h_1/h_2)^{0.5}]^2}$$

when $\eta = \eta_P = 0.5 = \eta_{\max}/2$.

4. Numerical examples and discussions

For the convenience of calculation and analysis, $h_1 = h_2$ is set and the following dimensionless variables and constants
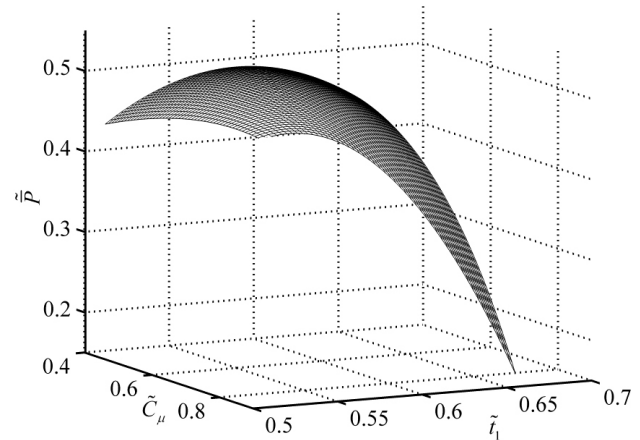

FIGURE 2. The average power output of the chemical engine $\tilde{\bar{P}}$ versus the parameters $\tilde{C}_\mu$ and $\tilde{t}_1$ ($c_{10} = 0.8$).
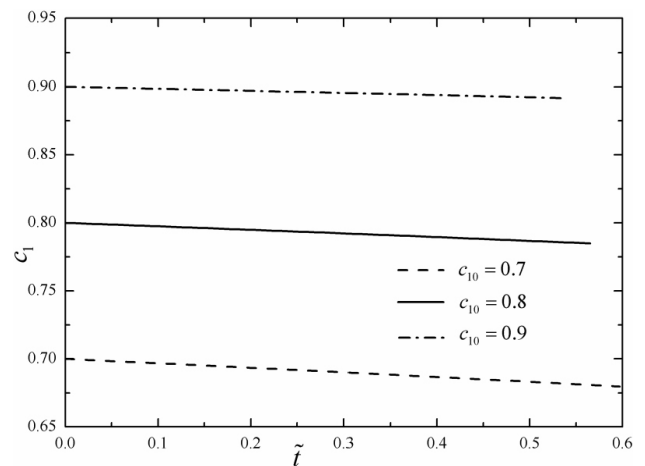

FIGURE 3. The optimal concentration profile of the key component B_1 in the finite high-chemical-potential reservoir.

TABLE I. Some operational parameters of the chemical engine corresponding to the optimal cycle configuration for maximum work output.

Case	$\tilde{t}_1$	$\tilde{C}_\mu$	$c_1(\tilde{t}_1)$	$c_{1'}(0)$	$c_{1'}(\tilde{t}_1)$	$c_{2'}$	$\tilde{\bar{P}}$	η
$c_{10} = 0.7$	0.5970	0.5312	0.6797	0.4115	0.3996	0.2196	0.4290	0.5066
$c_{10} = 0.8$	0.5652	0.6206	0.7849	0.4301	0.4220	0.2240	0.5109	0.5052
$c_{10} = 0.9$	0.5333	0.7170	0.8917	0.4394	0.4354	0.2269	0.5950	0.5032

are defined:

$$\tilde{G}_{10} = \frac{G_{10}}{h_1 RT\tau}, \qquad \tilde{\mu}_{01} = \frac{\mu_{01}}{RT}, \qquad \tilde{\mu}_{02} = \frac{\mu_{02}}{RT},$$

$$\tilde{\bar{P}} = \frac{\bar{P}}{h_1 R^2 T^2}, \qquad \tilde{t} = \frac{t}{\tau}, \qquad \tilde{C}_\mu = \frac{C_\mu}{RT},$$

$$\tilde{\mu}_i = \frac{\mu_i}{RT} \qquad (i = 1, 2), \tag{57}$$

Then Eqs. (36) and (42) can be rewritten as

$$c_1(\tilde{t}) = \frac{1 - \tilde{G}_{10}(1 - c_{10})}{(\tilde{G}_{10} - \tilde{C}_\mu \tilde{t})}, \qquad 0 \le \tilde{t} \le \tilde{t}_1 \tag{58}$$

$$\tilde{\bar{P}} = \tilde{C}_\mu \ln\left(\frac{\tilde{G}_{10}c_{10} - \tilde{C}_\mu \tilde{t}_1}{\tilde{G}_{10} - \tilde{C}_\mu \tilde{t}_1}\right) + \tilde{G}_{10} \ln\left(\frac{\tilde{G}_{10} - \tilde{C}_\mu \tilde{t}_1}{\tilde{G}_{10}}\right)$$

$$- \tilde{G}_{10}c_{10} \ln\left(\frac{\tilde{G}_{10}c_{10} - \tilde{C}_\mu \tilde{t}_1}{\tilde{G}_{10}c_{10}}\right)$$

$$+ \tilde{C}_\mu \tilde{t}_1 (\Delta\tilde{\mu}_0 - \ln c_2) - \tilde{C}_\mu^2 \frac{\tilde{t}_1}{1 - \tilde{t}_1}. \tag{59}$$

The following parameters are used in the calculations: $\tilde{G}_{10} = 5$, $\tilde{\mu}_{01} = 1.5$, $\tilde{\mu}_{02} = 0.5$, and $c_2 = 0.1$. In order to analyze the effects of the concentration changes of the key component B_1 in the high-chemical-potential on the optimal cycle configuration of the chemical engine for maximum work output, the values of 0.7, 0.8 and 0.9 are set for c_{10}, respectively. Figure 2 shows the average power output ($\tilde{\bar{P}}$) of the chemical engine versus the parameters $\tilde{C}_\mu$ and $\tilde{t}_1$ ($c_{10} = 0.8$). From Fig. 2, one can see that there is a maximum value for $\tilde{\bar{P}}$ as a function of $\tilde{C}_\mu$ and $\tilde{t}_1$. Table I lists some operational parameters of the chemical engine corresponding to the optimal cycle configuration for maximum work output (or maximum average power output). From Table I, one can see that with the increase of the concentration of the key component B_1 in the finite high-chemical-potential reservoir, the optimal time ($\tilde{t}_1$) spent on the mass transfer between the finite high-chemical-potential reservoir and the working fluid of the chemical engine decreases, the concentrations ($c_{1'}(0)$ and $c_{1'}(\tilde{t}_1)$) of the key component B_1 in the working fluid increase, and the concentration ($c_{2'}$) of the key component B_2 in the working fluid increases. Besides, with the increase of c_{10}, the average power output ($\tilde{\bar{P}}$) of the chemical engine increases; however, the efficiency η decreases. Also from Table II, the efficiency η is a bit larger than 0.5 for different values of c_{10}. For the given numerical example herein, the efficiency of the isothermal endoreversible chemical engine with the finite high-chemical- potential reservoir and the

linear mass transfer law corresponding to the optimal cycle configuration for maximum work output is larger than that with infinite mass reservoirs and the same mass transfer law.

Figures 3 and 4 show the optimal concentration and the optimal chemical potential profiles of the key component B_1 in the finite high-chemical-potential reservoir, respectively. From Fig. 3, for the cases with different values of c_{10}, when the working fluid of the chemical engine absorbs mass from the high-chemical-potential reservoir, the concentration of the key component B_1 in the high-chemical-potential reservoir decreases with the increase in time $\tilde{t}$. However, the concentration $c_1(\tilde{t})$ changes non-linearly with time $\tilde{t}$ from Eq. (58). Comparing Fig. 3 with Fig. 4, one can see that the optimal chemical potential profile of the key component B_1 in the finite high-chemical-potential reservoir is very similar to its optimal concentration profile, which is due to the fact that they follow the equation $\mu_1(c_1) = \mu_{01}(P,T) + RT \ln c_1$.

Figure 5 shows the optimal concentration configurations of the two key components in the working fluid of the isothermal endoreversible chemical engine for maximum work output. Ondrechen *et al.* [21] showed that the optimal configuration of endoreversible heat engine operating between a finite heat source and an infinite heat sink for maximum work output with Newton's heat transfer law in the heat transfer processes is a generalized Carnot heat engine in which the temperatures of the heat source and the working fluid change exponentially with time and the ratio of the temperatures of the working fluid and the heat source is a constant, and the temperature of the working fluid at the low-temperature side is also a constant. This paper shows that the optimal configuration of the isothermal endoreversible chemical engine operating between a finite high-chemical-potential reservoir and an infinite low-chemical-potential reservoir for maximum work output with linear mass-transfer law in the mass transfer processes is an isothermal endoreversible chemical engine in which the chemical potential (concentration) of the key component in the finitehigh-chemical-potential mass reservoir and that in the working fluid change nonlinearly with time and the difference in chemical potentials (ratio of the concentrations) between the key component in the finite mass reservoir and the working fluid is a constant, and the chemical potential (concentration) of the key component in the working fluid at the low chemical potential side is also a constant, as shown in Fig. 5. Refs. 21 and 50 showed that the optimal configurations of any heat engines were achieved in a heat engine by operating it so as to keep the entropy generation rate constant along each heat transfer branch. From
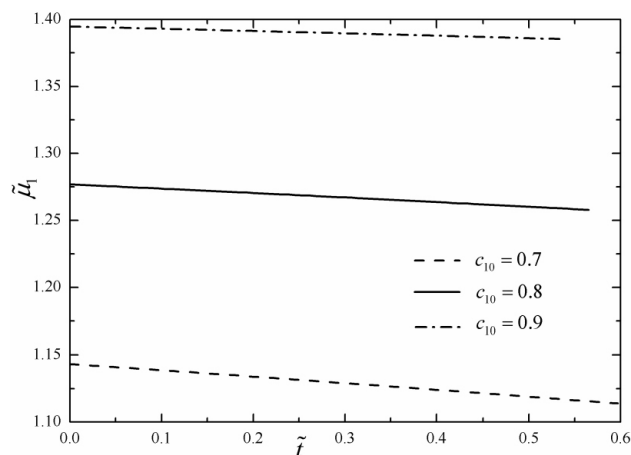
FIGURE 4. The optimal chemical potential profile of the key component B_1 in the finite high-chemical-potential reservoir.
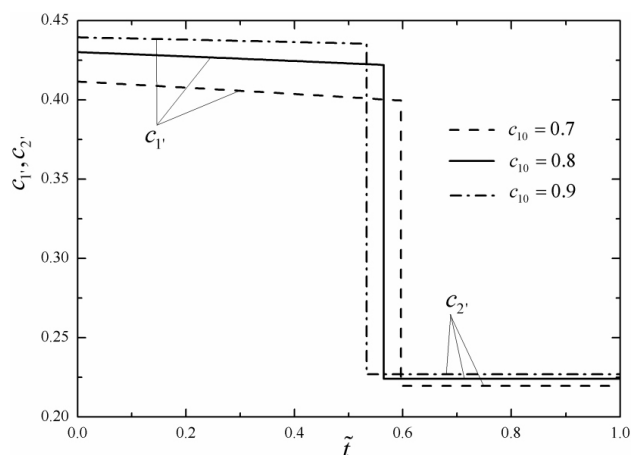

FIGURE 5. The optimal concentration configurations of the two key components in the working fluid of the isothermal endoreversible chemical engine for maximum work output.

Eqs. (27) and (28), one can see that the entropy generation rate along each mass transfer branch of the optimal cycle configuration of the chemical engine is also a constant. This is the similarity between the optimal cycle configuration of the endoreversible heat engine and that of the isothermal endoreversible chemical engine.

5. Conclusion

On the basis of the analogies of similar studies for endoreversible heat engines [21] and with the method of analogy and transplanting, a model of an isothermal endoreversible chemical engine operating between a finite high-chemical-

potential reservoir and an infinite low- chemical-potential reservoir in which the mass transfer between the working fluid and the mass reservoirs obeys the linear mass-transfer law [$g \propto \Delta\mu$], is put forward in this paper. Optimal control theory is applied to determine the optimal cycle configuration corresponding to the maximum work output per cycle for the fixed total cycle time. The optimal cycle configuration is an isothermal endoreversible chemical engine cycle in which the chemical potential (concentration) of the key component in the finite high-chemical-potential mass reservoir and that in the working fluid change nonlinearly with time, the difference in the chemical potentials (ratio of the concentrations) of the key component between the finite mass reservoir and the working fluid is a constant, and the chemical potential (the concentration) of the key component in the working fluid at the low chemical potential side is also a constant. Numerical examples are provided, and the effects of the concentration changes of the key component in the infinite high-chemical-potential reservoir on the optimal cycle configuration of the chemical engine are analyzed. The obtained results are compared with those obtained for an endoreversible heat engine operating between a finite heat source and an infinite heat sink with Newton's heat transfer law in the heat transfer processes.

The subject studied in this paper is an isothermal chemical engine with finite mass reservoirs, which is more general compared to the common isothermal endoreversible chemical engine with infinite mass reservoirs [26-39]. The idea and method used in this paper could be extended to research into the optimizing performances of two-mass-reservoir chemical pump [51-53], three-mass-reservoir chemical pump [54], three-mass-reservoir chemical transformer [55,56], four-mass-reservoir chemical pump [57,58] and four-mass-reservoir chemical transformer [59,60]. 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 and so on.

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