Estimation of productivity, efficiency, and entropy production for cyclic separation processes with a distributed working fluid

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The upper bound on average productivity and efficiency and the lower bounds on entropy production of an irreversible cyclic separation process with space-variable temperature and chemical-potential reservoirs are calculated via the generalized formalism of finite-time thermodynamics. The working fluid is described by partial differential equations, containing controls and parameters in the boundary conditions.

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I. INTRODUCTION

Some of the most useful and important results of thermodynamics are criteria of performance of real processes, and the natural limits which those real processes may attain. These limits and the corresponding regimes of operation that yield near-optimal performance serve as patterns for designing the most effective technological schemes. Thermodynamics creates a bridge between science and engineering in this context; the derivation of criteria and limits, and the demonstration of the feasibility of their evaluation, come from the science side, and their application to the design of real systems and processes fall to engineering to implement. Here we determine criteria and limits of performance and demonstrate the feasibility of their evaluation for an important class of processes, namely cyclic separation processes. This work, in effect, builds the scientific side of the bridge and brings the subject to the stage at which it can be applied in engineering contexts.

The simplest, best understood criteria of performance come from classical thermodynamics. These are Carnot efficiencies, based on the performance of idealized, reversible processes, for which the duration of the process is infinite and the fluxes go to their limit of zero. The reversible model indeed provides unassailable but not necessarily useful criteria, simply because we normally design processes specifically to yield products at a predetermined rate. The constraint of a fixed, nonzero rate (or a minimum rate) sometimes imposes lower bounds to losses that reduce the optimal performance of a system well below the Carnot limit. Finite-time thermodynamics has been developed to provide limits of performance (or sometimes estimates of those limits) for processes operating within finite intervals or at a nonzero rate. Both criteria and limits have been obtained for a variety of systems [1–21,23–27]. Most of these results have been for engines of one or another sort. The criteria have included not only efficiency but also average power, entropy generation, loss of availability, and even net revenue.

In most cases, finding the pathway in terms of time and the control variables of the system has entailed solving an optimal-control problem. Moreover these have mostly been of the so-called averaged type, that can be solved fairly easily. All the results cited except those in [16] were obtained for simplified, lumped-parameter models, without taking into account any effects of distributions of values of the variables. Here we address one generic class of processes, probably the furthest from optimal in its operation among all major classes of processes used in industry, in terms of thermodynamic criteria. It is well known that industrial separation processes are carried out very inefficiently from a thermodynamic viewpoint. The diffusive-mechanical, noncyclic separation process has been considered in [6,14,21]. Heat-driven separation processes were analyzed [17] and bounds, analogous to the bounds of the irreversible heat engine, were obtained for distributed systems, i.e. for systems with nonuniform values of their intensive variables. The cyclic separation processes were analyzed in [18,20] in the framework of the lumped-parameter model.

In this paper we consider heat-driven cyclic, diffusion-based separation processes. They differ from heat engines because the driving force of these processes is not only the temperature gradient but also the chemical potential gradient between the working body and reservoirs; moreover entropy production due to both heat and mass transfer is taken into account. This is a rather general type of diffusion-heat pump system which includes industrial absorption-stripper separation processes and some transport processes in biological systems. As a model we take the absorption-stripping process, which makes our problem no less general. Such a process is shown schematically in Fig. 1. The separation agent (liquid absorbent) circulates in a closed loop. It cools out and absorbs the key component from the gas mixture during contact in the absorber and heats up and recovers the objective component in the stripper during contact with stripping vapor. We will designate the source of the input gas and the receiver of the output vapor as reservoirs, and the absorbent in analogy with heat engines as the working body. The working fluid is described by the equations of a viscous, nonisothermal two-component fluid. Boundary conditions for these equations contain switching controls $v_a(t)$ and $v_s(t)$. These functions of time t regulate the finite-rate heat and mass transfer be-

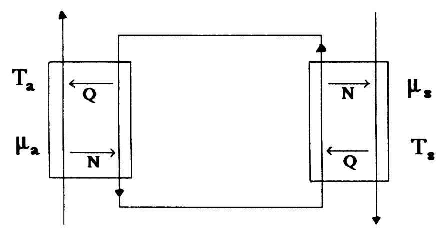

FIG. 1. The scheme of absorption-stripping separation process.

tween the working fluid and two reservoirs. When $v_s(t)=1$ the reservoir with high temperature and low chemical potential and the working fluid are in contact and exchange energy and substance; when $v_s(t)=0$ there is no exchange between them. When $v_a(t)=1$ the reservoir with low temperature and high chemical potential and the working fluid are in contact and exchange energy and substance; when $v_a(t)=0$ there is no exchange between them. We assume here that $v_s(t)v_a(t)=0$. The assumption implies that the working fluid cannot be in contact with two reservoirs simultaneously. The initial and final states of the working fluid need not be equilibrium states. We will optimize our objectives on the set of the weakly periodic processes which are defined as processes for which $E(0)=E(\tau)$, $K(0)=K(\tau)$, $S(0)=S(\tau)$, and $G(0)=G(\tau)$, where $E(t)$, $K(t)$, $S(t)$, and $G(t)$ are the total internal and kinetic energy, total entropy, and total mass of the working fluid, and $\tau>0$ is the period of the process. In a weakly periodic process, the integral values of extensive variables are the same at the beginning and end of each "cycle" but the local values of these quantities need not be the same. Hence a process which involves turbulent flow can be weakly periodic.

The bounds are obtained in algorithmic form; that is, the complicated variational problem, not solvable by the standard methods, is transformed into set of nonlinear algebraic equations that can be solved easily via routine numerical methods.

II. DESCRIPTION OF THE MODEL

The distributed-parameter irreversible cyclic separation process is described by the equations [22]

$$
\begin{aligned}
&\frac{\partial \rho}{\partial t}+\frac{\partial}{\partial \xi_j}(\rho u_j)=0 ,\\
&\frac{\partial}{\partial t}(\rho c)+\frac{\partial}{\partial \xi_j}(\rho c u_j+n_j)=0 ,\\
&\rho\left[\frac{\partial u_i}{\partial t}+u_k\frac{\partial u_i}{\partial \xi_k}\right]=\frac{\partial}{\partial \xi_k}(\sigma_{ik}-p) ,\\
&\rho T\left[\frac{\partial s}{\partial t}+u_k\frac{\partial s}{\partial \xi_k}\right]=\sigma_{ik}\frac{\partial u_i}{\partial \xi_k}-\frac{\partial}{\partial \xi_i}(q_i-\mu n_i)-n_i\frac{\partial \mu}{\partial \xi_i} ,
\end{aligned}
\tag{1}
$$

and the boundary conditions for gas-liquid problem are

$$
\begin{aligned}
&q_j\nu_j=Qv ,\\
&(u_j-D_j)\nu_j=0 ,\\
&n_j\nu_j=Nv ,\\
&\sigma_{ij}\nu_j=P\nu_i,\quad i=1,2,3 .
\end{aligned}
\tag{2}
$$

This and further summation is understood over the repeated indices. The following analysis is not sensitive to the form of boundary conditions. The second and fourth may have different form, e.g., $nxv=0$ for the liquid-solid problem. However, the first and third conditions are general: they specify the local balance of heat and mass. The quantities $\rho(t,\xi)$, $c(t,\xi)$, $s(t,\xi)$, and $u_i(t,\xi)$, $i=1,2$, and 3, are the total mass density, concentration of the key component, entropy density, and velocity, respectively; T, p, and μ are the temperature, pressure, and chemical potential, and

$$\sigma_{ik}=\eta\left[\frac{\partial u_i}{\partial \xi_k}+\frac{\partial u_k}{\partial \xi_i}-\frac{2}{3}\delta_{ik}\frac{\partial u_l}{\partial \xi_l}\right]+\zeta\frac{\partial u_l}{\partial \xi_l}\delta_{ik}$$

is the viscous stress tensor, η and ζ are given positive constants, $\delta_{ij}=1$ when $i=j$, $\delta_{ij}=0$ when $i\neq j$, i and $j=1,2$, and 3, and $i=1,2$, and 3. The heat and mass fluxes in the fluids are q_i and n_i. The equation system (1) is closed with the help of given functions $T=T(s,\rho,c)$, $p=p(s,\rho,c)$, $\mu=\mu(s,\rho,c)$, $q_j(T,\nabla T,c,\nabla c)$, and $n_j(T,\nabla T,c,\nabla c)$. In (2), $D_j(t,\xi)$ and $P(t,\xi)$ are the given boundary velocity components and the pressure on the boundary, $\partial\Omega$ is the boundary of the working fluid, $\nu(t,\xi)$ is the outer normal vector at the point $\xi\in\partial\Omega$, and $v(t,\xi)$ is a switching function regulating heat and mass transfer between the working fluid and two reservoirs. It is assumed that it consists only of the time-dependent switching function $v_s(t)$ on the contact surface in the stripper, and $v_a(t)$ at the contact surface in absorber. That is, it has the form $v(t,\xi)=v_s(t)$ when $\xi\in A_s$, $v(t,\xi)=v_a(t)$ when $\xi\in A_a$, and $v(t,\xi)=0$ when $\xi\in A_a\cup A_s$, where A_a and A_s are the parts of the boundary $\partial\Omega(t)$, in contact, respectively, with the stripper and absorber reservoirs. Functions Q and N have the form

$$
\begin{aligned}
&Q_R=\lambda_R\left[\frac{1}{T_R}-\frac{1}{T}\right]+\alpha_R\left[\frac{\mu_R}{T_R}-\frac{\mu}{T}\right] ,\\
&N_R=\alpha_a\left[\frac{1}{T_R}-\frac{1}{T}\right]+k_R\left[\frac{\mu_R}{T_R}-\frac{\mu}{T}\right] .
\end{aligned}
\tag{3}
$$

When $\xi\in A_s$, $T_R(\xi)=T_s(\xi)$, $\mu_R(\xi)=\mu_s(\xi)$, $\lambda_R(\xi)=\lambda_s(\xi)$, $\alpha_R(\xi)=\alpha_a(\xi)$, and $k_R(\xi)=k_s(\xi)$, and when $\xi\in A_a$, $T_R(\xi)=T_a(\xi)$, $\mu_R(\xi)=\mu_a(\xi)$, $\lambda_R(\xi)=\lambda_a(\xi)$, $\alpha_R(\xi)=\alpha_a(\xi)$, and $k_R(\xi)=k_a(\xi)$. Here $\lambda_s(\xi)$, $\lambda_a(\xi)$, $\alpha_s(\xi)$, $\alpha_a(\xi)$, $k_s(\xi)$, and $k_a(\xi)$ are coefficients; $T_s(\xi)$, $T_a(\xi)$, $\mu_s(\xi)$ and $\mu_a(\xi)$ are temperatures and chemical potentials of reservoirs.

Controls $v_s(t)$ and $v_a(t)$ are considered admissible if $0\le v_s(t)\le 1$, $0\le v_a(t)\le 1$, and $v_s(t)v_a(t)=0$ and there exists a solution of (1) and (2) satisfying the conditions $E(0)=E(\tau)$, $K(0)=K(\tau)$, $S(0)=S(\tau)$, $G(0)=G(\tau)$, $c(t,\xi)\ge 0$, and $\rho(t,\xi)\ge 0$. Here $E(t)=\int_\Omega \epsilon\rho\, d\xi$ and

$K(t)=\int_{\Omega}(\rho u^2/2)d\xi$ are the total internal and kinetic energies, respectively, $S(t)=\int_{\Omega}s\rho\, d\xi$ is the total entropy, and $G(t)=\int_{\Omega}\rho\, d\xi$ is the total mass of the working fluid. The given function $\epsilon(s,\rho,c)$ is specific internal energy of absorbent.

The average productivity of the system is defined as a generalized power, i.e.,

$$\mathcal{P}=\frac{1}{\tau}\int_0^{\tau}\left[\int_{A_a}v_a N_a da\right]dt \ , \tag{4}$$

the average heat consumption

$$\mathcal{Q}=\frac{1}{\tau}\int_0^{\tau}\left[\int_{A_s}v_s Q_s da\right]dt \ , \tag{5}$$

the efficiency is

$$\eta_1=\frac{\mathcal{P}}{\mathcal{Q}} \ ,$$

and average entropy production is

$$\mathcal{S}=\frac{1}{\tau}\int_0^{\tau}\left\{\int_{A_s}^{\tau}v_s\left[Q_s\left[\frac{1}{T}-\frac{1}{T_s}\right]+N_s\left[\frac{\mu_s}{T_s}-\frac{\mu}{T}\right]\right]da + \int_{A_s}v_a\left[Q_a\left[\frac{1}{T}-\frac{1}{T_a}\right] + N_a\left[\frac{\mu_a}{T_a}-\frac{\mu}{T}\right]\right]da\right\}dt \tag{6}$$

consisting of both heat and mass transfer contributions. Here $\tau>0$ is the period time.

Problem 1: to find an upper bound of $\mathcal{P}_{\max}$ on the solution of (1) and (2) which is valid for all admissible controls.

Problem 2: to find an upper bound of efficiency $\eta_{1_{\max}}$ with given productivity. This is equivalent to calculation of the lower bound of $\mathcal{Q}$ on the solution of (1) and (2) which is valid for all admissible controls such that the average productivity has a given value $\mathfrak{P}:\mathcal{P}=\mathfrak{P}$.

Problem 3: to find a lower bound of $\mathcal{S}_{\min}$ on the solution of (1) and (2) which is valid for all admissible controls such that the average productivity has a given value $\mathfrak{P}:\mathcal{P}=\mathfrak{P}$.

III. ENTROPY, ENERGY, AND MASS BALANCES AND CONSTRAINT BREAKING

Any solution of (1) and (2) with admissible control obeys the following equations of heat, entropy, and mass balance for the working body:

$$\int_0^{\tau}\left[\int_{A_a}Q_a v_a da+\int_{A_s}Q_s v_s da\right]dt+\delta_1^2=0 \ , \tag{7a}$$

$$\int_0^{\tau}\left[\int_{A_s}v_s\left[\frac{Q_s}{T}-\frac{N_s\mu}{T}\right]da + \int_{A_a}v_a\left[\frac{Q_a}{T}-\frac{N_a\mu}{T}\right]da\right]dt+\delta_2^2=0 \ , \tag{7b}$$

$$\int_0^{\tau}\left[\int_{A_s}N_s v_s da+\int_{A_a}N_a v_a da\right]dt=0 \ , \tag{7c}$$

where

$$\delta_1^2=\int_0^{\tau}\int_{\Omega}\eta\left[\frac{\partial u_i}{\partial \xi_k}+\frac{\partial u_k}{\partial \xi_i}\right]^2 d\xi\, dt \ , \tag{7d}$$

$$\delta_2^2=\int_0^{\tau}\int_{\Omega}\left[\frac{\eta}{2T}\left[\frac{\partial u_i}{\partial \xi_k}+\frac{\partial u_k}{\partial \xi_i}-\tfrac{2}{3}\delta_{ik}\frac{\partial u_l}{\partial \xi_l}\right]^2 + \frac{\zeta}{T}\left[\frac{\partial u_l}{\partial \xi_l}\right]^2\right]d\xi\, dt \tag{7e}$$

are the total heat and entropy production in the working fluid during the cycle.

Using expressions for Q and N, constraints (7a)–(7c) can be rewritten in the form

$$\int_0^{\tau}\left[\int_{A_a}Q_s v_s da+\int_{A_a}Q_a v_a da\right]dt+\delta_1^2=0 \ , \tag{8a}$$

$$\int_0^{\tau}\left[\int_{A_s}v_s\left[\frac{Q_s^2}{\tilde{\lambda}_s}+\frac{N_s^2}{\tilde{k}_s}+Q_s u_{1s}-N_s u_{2_s}-N_s Q_s\tilde{\alpha}_s\right]da + \int_{A_a}v_a\left[\frac{Q_a^2}{\tilde{\lambda}_a}+\frac{N_a^2}{\tilde{k}_a}+Q_a u_{1a}-N_a u_{2_a} - N_a Q_a\tilde{\alpha}_a\right]da\right]dt+\delta_2^2=0 \ , \tag{8b}$$

$$\int_0^{\tau}\left[\int_{A_s}N_s v_s da+\int_{A_a}N_a v_a da\right]dt=0 \ . \tag{8c}$$

where

$$\tilde{\lambda}_i=\lambda_i-\frac{\alpha_i^2}{k_i}, \quad \tilde{k}_i=k_i-\frac{\alpha_i^2}{\lambda_i}, \quad \tilde{\alpha}_i=\frac{2\alpha_i}{k_i\lambda_i-\alpha_i^2} \ ;$$

$$u_{1i}=\frac{1}{T_i}, \quad u_{2i}=\frac{\mu_i}{T_i}, \quad i=a,s \ .$$

The average entropy production can be rewritten as

$$\mathcal{S}=\frac{1}{\tau}\int_0^{\tau}\left[\int_{A_s}v_s\left[\frac{Q_s^2}{\tilde{\lambda}_s}+\frac{N_s^2}{\tilde{k}_s}-2\tilde{\alpha}_s N_s Q_s\right]da + \int_{A_a}v_a\left[\frac{Q_s^2}{\tilde{\lambda}_s}+\frac{N_s^2}{\tilde{k}_s}-2\tilde{\alpha}_s N_s Q_s\right]da\right]dt \ . \tag{9}$$

Instead of solving problems 1 and 2 directly we will solve them by breaking constraints, and replacing the problems at each stage with problems with the same objective and extended set of admissible states. Let us illustrate it for problem 1.

First we consider problem 1′: to find an upper bound of (4) based on the solution of system (7a)–(7d) over the range of admissible parameters. All admissible solutions obey (7a)–(7d), but (1), (2), and (7a)–(7d) are not equivalent. Eqs. (7a)–(7d) can have additional solutions within the admissible range of parameters. Therefore any solution of problem 1′ is greater than or equal to the solution of problem 1. In other words the solution of problem 1′ gives an upper bound for the solution of problem 1.

Second we break the constraints (7d), $T=T(s,\rho,c)$, and $\mu=\mu(s,\rho,c)$ and consider fluxes Q and N between working body and reservoirs and total entropy and heat production in the working fluid and heat and mass production δ_1 and δ_2 as new controls. Thus we obtain an estimate of (4) by solving the simplified optimal control problem 1″: to maximize (4) subject to constraints (8a)–(8c) over the set of controls v_s, v_a, N, Q, δ_1, and δ_2.

Problem 2″ is formulated similarly to minimize (5) subject to (8a)–(8c) and

$$\frac{1}{\tau}\int_0^\tau \left[\int_{A_a} v_a N_a da\right] dt = \mathfrak{P} ,$$

with respect to v_s, v_a, N, Q, δ_1, and δ_2. And problem 3″ is to minimize (9) subject to the same constraints as problem 2″.

IV. LAGRANGE MULTIPLIERS AND SOLUTION OF AVERAGED PROBLEMS

Problems 1″–3″ are typical averaged problems. Instead of using the general apparatus of averaged optimal-control problems [5,18], we will derive the necessary conditions of optimality directly for our problem, which is much easier in our particular case. We will use the method of Lagrange multipliers.

Let us note that for problem 1″ the optimal $v_a(t)$ or $v_s(t)$ can take the value 0 or 1 only because problem 1″ is linear with respect to v. Another feature of this problem is that the objective and constraint for two different $v(t)$'s which have equal total durations of contacts with both reservoirs are equal. Therefore we can take $v_a(t)=1, v_s(t)=0$ for $t\in[0,\tau_1]$, and $v_a(t)=0, v_s(t)=1$ for $t\in[\tau_1,\tau]$ without loss of generality, and carry out maximization on τ_1 instead of maximization on v_a, v_s.

The Lagrange functional R of problem 1″ has the form

$$R(\lambda_1,\lambda_2,\lambda_3,N,Q,\tau_1)=\tau_1\left\{\int_{A_a}\left[N_a+\lambda_1\left[\frac{Q_a^2}{\tilde{\lambda}_a}+\frac{N_a^2}{\tilde{k}_a}+Q_a u_{1a}-N_a u_{2_a}-N_a Q_a \tilde{\alpha}_a\right]+\lambda_2 Q_a+\lambda_3 N_a\right]da\right\}$$
$$+(\tau-\tau_1)\left\{\int_{A_s}\left[\lambda_1\left[\frac{Q_s^2}{\tilde{\lambda}_s}+\frac{N_s^2}{\tilde{k}_s}+Q_s u_{1s}-N_s u_{2_s}-N_s Q_s \tilde{\alpha}_s\right]+\lambda_2 Q_s+\lambda_3 N_s\right]da\right\}+\lambda_1\delta_1^2+\lambda_2\delta_2^2 . \tag{10}$$

Here λ_1, λ_2, and λ_3 are Lagrange multipliers.

The maximum of R with respect to δ_1 and δ_2 is attained for $\delta_1=0$, $\delta_2=0$, and $\lambda_1<0$, and $\lambda_2<0$ (otherwise R is not bounded).

The condition of maximum R on τ_1 gives

$$\int_{A_a}\left[N_a+\lambda_1\left[\frac{Q_a^2}{\tilde{\lambda}_a}+\frac{N_a^2}{\tilde{k}_a}+Q_a u_{1a}-N_a u_{2_a}-N_a Q_a \tilde{\alpha}_a\right]+\lambda_2 Q_a+\lambda_3 N_a\right]da$$
$$=\int_{A_s}\left[\lambda_1\left[\frac{Q_s^2}{\tilde{\lambda}_s}+\frac{N_s^2}{\tilde{k}_s}+Q_s u_{1s}-N_s u_{2_s}-N_s Q_s \tilde{\alpha}_s\right]+\lambda_2 Q_s+\lambda_3 N_s\right]da , \tag{11}$$

and with respect to variables $N_i(t,\xi)$ and $Q_i(t,\xi)$, $i=a$ and s can be solved analytically:

$$N_a^* = \frac{[2+2\lambda_3+\tilde{\alpha}_a\tilde{\lambda}_a\lambda_2+\lambda_1(\tilde{\alpha}_a\tilde{\lambda}_a u_{1a}-2u_{2a})]\tilde{k}_a}{\lambda_1 O_a} ,$$
$$Q_a^* = \frac{[2\lambda_2+\tilde{\alpha}_a\tilde{k}_a+\tilde{\lambda}_a\lambda_3\tilde{k}_a+\lambda_1(-\tilde{\alpha}_a\tilde{k}_a u_{2a}+2u_{1a})]\tilde{l}_a}{\lambda_1 O_a} ,$$
$$N_s^* = \frac{[2\lambda_3+\tilde{\alpha}_s\tilde{\lambda}_s\lambda_2+\lambda_1(\tilde{\alpha}_s\tilde{\lambda}_s u_{1s}-2u_{2s})]\tilde{k}_s}{\lambda_1 O_s} ,$$
$$Q_s^* = \frac{[2\lambda_2+\tilde{\alpha}_s\tilde{k}_s+\tilde{\lambda}_s\lambda_3\tilde{k}_s+\lambda_1(-\tilde{\alpha}_s\tilde{k}_s u_{2s}+2u_{1s})]\tilde{l}_s}{\lambda_1 O_s} , \tag{12}$$

where

$$O_i=\tilde{\alpha}_i^2\tilde{k}_i\tilde{\lambda}_i-4, \quad i=a,s .$$

Substitution of (12) into (8a)–(8c) and (11) gives optimality conditions for problem 1″ in the form of closed set of four equations for finding λ_1, λ_2, λ_3, and $\gamma=\tau_1/\tau$ (note that these equations do not depend on τ; that is, the optimal regime is universal for all values of τ):

$$(B_a - B_s)\lambda_3^2 + (C_a - C_s)\lambda_2^2 - (D_a - D_s)\lambda_1^2 + (F_a - F_s)\lambda_2\lambda_3 + (M_a - M_s)\lambda_1\lambda_3 + (L_a - L_s)\lambda_1\lambda_2 + 2B_a\lambda_3 + F_a\lambda_2 + M_a\lambda_1 + B_a = 0 ,$$

$$[\gamma B_a + (1-\gamma)B_s]\lambda_3^2 + [\gamma C_a + (1-\gamma)C_s]\lambda_2^2 + [\gamma D_a + (1-\gamma)D_s]\lambda_1^2 + [\gamma F_a + (1-\gamma)F_s]\lambda_2\lambda_3 + 2B_a\gamma\lambda_3 + F_a\gamma\lambda_2 + \gamma B_a = 0 ,$$

$$[\gamma F_a + (1-\gamma)F_s]\lambda_3 + 2[\gamma C_a + (1-\gamma)C_s]\lambda_2 + [\gamma L_a + (1-\gamma)L_s]\lambda_1 + \gamma F_a = 0 , \tag{13}$$

$$2[\gamma B_a + (1-\gamma)B_s]\lambda_3 + [\gamma F_a + (1-\gamma)F_s]\lambda_2 + [\gamma M_a + (1-\gamma)M_a]\lambda_1 + 2\gamma B_a = 0 ,$$

where $\gamma \in [0,1]$, $\lambda_1 < 0$, $\lambda_2 < 0$, and

$$B_i = \int_{A_i} \frac{\tilde{k}_i}{O_i} da , \quad C_i = \int_{A_i} \frac{\tilde{\lambda}_i}{O_i} da , \quad D_i = -\int_{A_i} \frac{\tilde{\lambda}_i u_{1i}^2 + \tilde{k}_i u_{2i}^2 - \tilde{\alpha}_i \tilde{k}_i \tilde{\lambda}_i u_{1i} u_{2i}}{O_i} da ,$$

$$F_i = \int_{A_i} \frac{\tilde{\lambda}_i \tilde{\alpha}_i \tilde{k}_i}{O_i} da , \quad L_i = \int_{A_i} \tilde{\lambda}_i \frac{2u_{1i} - \tilde{\alpha}_i \tilde{k}_i u_{2i}}{O_i} da , \quad M_i = \int_{A_i} \tilde{k}_i \frac{\tilde{\alpha}_i \tilde{\lambda}_i u_{1i} - 2u_{2i}}{O_i} da .$$

The bound on $\mathcal{P}$ is expressed in terms of the roots of (13) λ_1^*, λ_2^*, λ_3^*, and γ^*:

$$\mathcal{P}_{\max} = \frac{\gamma^*[2B_a(1+\lambda_3^*) + F_a\lambda_2^* + M_a\lambda_1^*]}{\lambda_1^*} , \tag{14}$$

which corresponds to the efficiency

$$\eta_1 = \frac{\gamma^*(2B_a(1+\lambda_3^*) + F_a\lambda_2^* + M_a\lambda_1^*)}{(1-\gamma^*)(F_s\lambda_3^* + 2C_s\lambda_2^* + L_s\lambda_1^*)} . \tag{15}$$

In the general case, the nonlinear set (13) can be solved only numerically. However, the case in which reservoir parameters T_i, μ_i, and $i = a$, and s do not depend on ξ, the coefficients of mass and heat transfer for absorber and stripper are constant and equal ($\alpha_a = \alpha_s = \alpha$, $k_a = k_s = k$, and $\lambda_a = \lambda_s = \lambda$), and the contact areas are equal, i.e., $A_a = A_s$ can be solved analytically. The following expression is obtained for the bound on $\mathcal{P}$:

$$\mathcal{P}_{\max} = \frac{\tilde{k}\tilde{\lambda}(u_{1a} - u_{1s})^2 A_a}{2(\tilde{\alpha}\tilde{\lambda}\tilde{k}(u_{1a} - u_{1s}) + 2\tilde{k}(u_{2s} - u_{2a}) + 2\sqrt{DS})} , \tag{16}$$

with efficiency

$$\eta_1 = \frac{u_{1a} - u_{1s}}{(u_{2s} - u_{2a}) + \left[1 + \frac{\tilde{\lambda}(u_{1a} - u_{1s})^2}{\tilde{k}(u_{2s} - u_{2a})^2} + \frac{\tilde{\lambda}\tilde{\alpha}(u_{1a} - u_{1s})}{(u_{2s} - u_{2a})}\right]^{1/2}} , \tag{17}$$

where

$$DS = \tilde{k}[\tilde{k}(u_{2s} - u_{2a})^2 + \tilde{\lambda}(u_{1a} - u_{1s})^2 + \tilde{\lambda}\tilde{\alpha}\tilde{k}(u_{2s} - u_{2a})(u_{1a} - u_{1s})] .$$

For problem 2″, in a similar way, we obtain optimality conditions in a form of a nonlinear set of equations with respect to λ_1, λ_2, λ_3, λ_4, and γ:

$$B_a\lambda_4^2 + (B_a - B_s)\lambda_3^2 + (C_a - C_s)\lambda_2^2 - (D_a - D_s)\lambda_1^2 + 2B_a\lambda_3\lambda_4 + F_a\lambda_2\lambda_4 + (F_a - F_s)\lambda_2\lambda_3 + (-\mathcal{P} + M_a)\lambda_1\lambda_4 + (M_a - M_s)\lambda_1\lambda_3 + (L_a - L_s)\lambda_1\lambda_2 + F_a\lambda_4 + 2C_a\lambda_2 + L_a\lambda_1 + C_a + F_a\lambda_3 = 0 ,$$

$$\gamma B_a\lambda_4^2 + [\gamma B_a + (1-\gamma)B_s]\lambda_3^2 + [\gamma C_a + (1-\gamma)C_s]\lambda_2^2 + [\gamma D_a + (1-\gamma)D_s]\lambda_1^2 + 2\gamma B_a\lambda_3\lambda_4 + \gamma F_a\lambda_2\lambda_4 + \gamma F_a(\lambda_3 + \lambda_4) + [\gamma F_a + (1-\gamma)F_s]\lambda_2\lambda_3 + 2C_a\gamma\lambda_2 + \gamma C_a = 0 ,$$

$$\gamma F_a\lambda_4 + [\gamma F_a + (1-\gamma)F_s]\lambda_3 + 2[\gamma C_a + (1-\gamma)C_s]\lambda_2 + [\gamma L_a + (1-\gamma)L_s]\lambda_1 + 2\gamma C_a = 0 , \tag{18}$$

$$2\gamma B_a\lambda_4 + 2[\gamma B_a + (1-\gamma)B_s]\lambda_3 + [\gamma F_a + (1-\gamma)F_s]\lambda_2 + [\gamma M_a + (1-\gamma)M_s]\lambda_1 + \gamma F_a = 0 ,$$

$$\gamma[2B_a(\lambda_4 + \lambda_3) + F_a\lambda_2 + M_a\lambda_1 + F_a] = \mathcal{P}\lambda_1 ,$$

where $\lambda_1 < 0$, $\lambda_2 < 0$, λ_3, and λ_4 are Lagrange multipliers.

The bound on $\mathcal{Q}$ is expressed in terms of the roots of (15) λ_1^*, λ_2^*, λ_3^*, λ_4^*, and γ^*:

$$\mathcal{Q}_{\min}=\frac{(1-\gamma^*)(F_s\lambda_3^*+2C_s\lambda_2^*+L_s\lambda_1^*)}{\lambda_1^*}\ , \tag{19}$$

and the bound on efficiency is

$$\eta_{1_{\max}}=\frac{\lambda_1^*P}{(1-\gamma^*)(F_s\lambda_3^*+2C_s\lambda_2^*+L_s\lambda_1^*)}\ . \tag{20}$$

Similarly problem 3″ is reduced to the set of equations for $\lambda_1<0$, $\lambda_2<0$, λ_3, λ_4, and $\gamma\in[0,1]$:

$$\begin{aligned}
&B_a\lambda_4^2+(B_a-B_s)\lambda_3^2+(C_a-C_s)\lambda_2^2-(D_a-D_s)\lambda_1^2+2B_a\lambda_3\lambda_4+F_a\lambda_2\lambda_4\\
&\qquad+(F_a-F_s)\lambda_2\lambda_3+(-\mathcal{P}+M_a)\lambda_1\lambda_4+(M_a-M_s)\lambda_1\lambda_3+(L_a-L_s)\lambda_1\lambda_2+\lambda_4\mathcal{P}=0\ ,\\
&\gamma B_a\lambda_4^2+[\gamma B_a+(1-\gamma)B_s]\lambda_3^2+[\gamma C_a+(1-\gamma)C_s]\lambda_2^2+[\gamma D_a+(1-\gamma)D_s]\lambda_1^2+2\gamma B_a\lambda_3\lambda_4+\gamma F_a\lambda_2\lambda_4+\gamma M_a(\lambda_3+\lambda_4)\\
&\qquad+(1-\gamma)M_s\lambda_3+[\gamma F_a+(1-\gamma)F_s]\lambda_2\lambda_3+[\gamma L_a+(1-\gamma)L_s]\lambda_2-2[D_a\gamma+(1-\gamma)D_s]\lambda_1=0\ ,\\
&\gamma F_a\lambda_4+[\gamma F_a+(1-\gamma)F_s]\lambda_3+2[\gamma C_a+(1-\gamma)C_s]\lambda_2+[\gamma L_a+(1-\gamma)L_s]\lambda_1=0\ ,\\
&2\gamma B_a\lambda_4+2[\gamma B_a+(1-\gamma)B_s]\lambda_3+[\gamma F_a+(1-\gamma)F_s]\lambda_2+[\gamma M_a+(1-\gamma)M_s]\lambda_1=0\ ,\\
&\gamma[2B_a(\lambda_4+\lambda_3)+F_a\lambda_2+M_a\lambda_1]=\mathcal{P}(-1+\lambda_1)\ ,
\end{aligned} \tag{21}$$

and the bound is expressed as

$$\begin{aligned}
\mathcal{S}_{\min}=&-[\gamma^*(B_a(\lambda_4^*+\lambda_3^*)^2+C_a\lambda_2^{*2}-D_a\lambda_1^{*2}+(F_a\lambda_2^*+2M_a\lambda_1^*)(\lambda_3^*+\lambda_4^*)+L_a\lambda_1^*\lambda_2^*)\\
&+(1-\gamma^*)(B_s\lambda_3^*)^2+C_s\lambda_2^{*2}-D_s\lambda_1^{*2}+(F_a\lambda_2^*+2M_a\lambda_1^*)\lambda_3^*]/(-1+\lambda_1^*)^2\ .
\end{aligned} \tag{22}$$

Analytical expressions for the solutions of problems 2″ and 3″ also have been obtained, only for the cases of equal and constant coefficients of heat and mass transfer, equal contact surfaces in absorber and stripper, and space-independent T_i, μ_i, and $i=a$, and s. For this special case these solutions coincide, but they do not in the general case. In the optimal regime, the working body spends equal time in the absorber and stripper ($\gamma^*=0.5$), and the mass fluxes are

$$-Q_a^*=Q_s^*=\frac{\tilde{\lambda}}{4}\left[u_{1a}-u_{1s}-2\tilde{\alpha}\tilde{\mathfrak{P}}-\left[(u_{1a}-u_{1s}-2\tilde{\alpha}\tilde{\mathfrak{P}})^2-\frac{8\tilde{\mathfrak{P}}}{\tilde{k}\tilde{\lambda}}[2\tilde{\mathfrak{P}}+\tilde{k}(u_{2s}-u_{2a})]\right]^{1/2}\right]\ ; \tag{23}$$

here $\tilde{\mathfrak{P}}=\mathfrak{P}/A_a$, and

$$\eta_{1_{\max}}=\frac{4\tilde{\mathfrak{P}}}{\tilde{\lambda}\left[u_{1a}-u_{1s}-2\tilde{\alpha}\tilde{\mathfrak{P}}+\left[(u_{1a}-u_{1s}-2\tilde{\alpha}\tilde{\mathfrak{P}})^2-\frac{8\tilde{\mathfrak{P}}}{\tilde{k}\tilde{\lambda}}[2\tilde{\mathfrak{P}}+\tilde{k}(u_{2s}-u_{2a})]\right]^{1/2}\right]}\ . \tag{24}$$

If $\mathfrak{P}\to 0$ the efficiency tends to the reversible value $\eta_{1_{\max}}\to(u_{1a}\to u_{1s})/(u_{2s}-uu_{2a})$.

V. ILLUSTRATIVE CALCULATIONS AND DISCUSSIONS

We computed bounds $\mathcal{Q}_{\min}$, $\eta_{1_{\max}}$, $\mathcal{S}_{\min}$, and $\mathcal{P}_{\max}$ for the absorption stripping of CO_2 by monoethanolamine solution from the waste industrial gases [19,20]. In this process $T_a=315$ K, $T_s=393$ K, and typical values of the concentrations of the key component in reservoirs are $c_a=0.22$ mol/mol, $C_s=0.80$ mol/mol; of the pressures $P_a=121.2$ kPa, $P_s=151.5$ kPa; of the areas $A_a=A_s=25$ m^2, and typical kinetic coefficients are $\alpha_a=\alpha_s=0$, $\lambda_a=\lambda_s=5\times10^6$ (kJ)s^{-1}M^{-2}K, and $k=5\times10^{-4}$ K(kmol)^2 (kJ)$^{-1}$s^{-1}M^{-2}. The following expression is used for calculation of the chemical potential of the reservoirs

$$\mu_i=\mu_i^0(T_i)+RT_i\ln c_i+RT_i\ln P_i,\quad i=a,s\ ,$$

where $\mu_i^0(T_i)$ is a standard chemical potential of the key component in the gas state, and R is a gas constant. It is assumed that $\mu_i^0(T_i)/T_i$ is constant.

Table I shows the parameters of the regimes with maximum efficiency (minimal heat consumption), maximal productivity, and the real process.

This work is illustrative of a transformation worth noting. The solution to the general problem posed here is expressed in a practical, computable form, but as an algorithmic rather than an analytic expression. A "solution"

TABLE I. Parameters of the regimes with maximum efficiency.

Parameters	Real process	Max efficiency	Max productivity
P (kmol/s)	0.05	0.05	0.166
Q (kJ/s)	123	1.556×10^3	19.7×10^3
η_1 (kmol/kJ)	0.001	3.2×10^{-5}	0.84×10^{-5}

to a general problem in physics is a statement, preferably terse, of how to find numerical values of physical variables for all possible cases falling in some domain of validity. Traditionally such "solutions" have been expressed in terms of functions, preferably in a closed form, stated in the language of conventional mathematics. Here the solution is general for its domain of validity but is expressed in terms of a set of commands for a computer, rather than in terms of traditional mathematical symbols. In one sense this distinction is trivial; in another sense, it reflects a significant enlargement of what we mean by "solving" a physical problem.

This is by no means a unique or new phenomenon. Algorithmic solutions are appearing ever more frequently, as people find such solutions to problems that have not yielded analytical solutions. We simply raise this point to sensitize the reader to the rich, new direction which scientific problem solving has taken. Insofar as a "solution" implies a useful recipe from which the outcome of any relevant case can be determined quantitatively, the power of modern computers has made the algorithmic solution just as valid and powerful as the traditional analytic solution. In some situations, algorithmic solutions are more efficient and provide more insight than their analytic counterparts.

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[1] F. L. Curzon and B. Ahlborn, Am. J. Phys. **43**, 22 (1975).
[2] B. Andresen, R. S. Berry, A. Nitzan, and P. Salamon, Phys. Rev. A **15**, 2086 (1977).
[3] P. Salamon and A. Nitzan, J. Chem. Phys. **74**, 3546 (1981).
[4] M. J. Ondrechen, B. Andresen, M. Mozurkewich, and R. S. Berry, Am. J. Phys. **498**, 681 (1981).
[5] L. I. Rozonoer and A. M. Tsirlin, Autom. Remote Control (USSR) **44**, 55 (1983).
[6] L. I. Rozonoer, in *Thermodynamics and Regulation of Biological Processes* 181 (de Gruler, Berlin, 1984).
[7] P. Salamon, Y. B. Band, and O. Kafri, J. Appl. Phys. **53**, 197 (1982).
[8] K. H. Hoffmann, S. J. Watowich, and R. S. Berry, J. Appl. Phys. **58**, 2125 (1985).
[9] M. J. Ondrechen, B. Andresen, and R. S. Berry, J. Chem. Phys. **72**, 5118 (1984).
[10] O. Mullins and R. S. Berry, J. Chem. Phys. **88**, 723 (1984).
[11] S. J. Watowich, K. H. Hoffman, and R. S. Berry, J. Appl. Phys. **58**, 2893 (1985).
[12] S. J. Watowich and R. S. Berry, J. Chem. Phys. **90**, 4624 (1986).
[13] J. W. Warner and R. S. Berry, J. Phys. Chem. **91**, 2216 (1987).
[14] G. R. Brown, S. Snow, B. Andresen, and P. Salamon, Phys. Rev. A **34**, 4370 (1986).
[15] M. H. Rubin, Phys. Rev. A **22**, 1741 (1980).
[16] V. N. Orlov and R. S. Berry, Phys. Rev. A **42**, 7230 (1990).
[17] V. N. Orlov and R. S. Berry, J. Phys. Chem. **95**, 5624 (1991).
[18] A. M. Tsirlin, *Cyclic Processes and Cyclic Regimes* (in Russian) (Mashinostroenie, Moscow, 1989).
[19] A. G. Kuznetsov, A. V. Rudenko, and A. M. Tsirlin, Avtom. Telemkh. (in Russian) **6**, 20 (1985).
[20] L. I. Rozonoer, A. V. Rudenko, and A. M. Tsirlin, Theor. Osn. Chim. Tech. (in Russian) **3**, 362 (1984).
[21] V. A. Mironova, A. M. Tsirlin, and U. B. Samarin, Chimicheskaia Promislenost (in Russian) **8**, 486 (1988).
[22] L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Pergamon, London, 1959).
[23] S. Sieniutycz and R. S. Berry, Phys. Rev. A **43**, 2807 (1991).
[24] S. Sieniutycz and R. S. Berry, Phys. Rev. A **46**, 6359 (1992).
[25] S. Sieniutycz and R. S. Berry, Phys. Rev. E **47**, 1765 (1993).
[26] P. T. Landsberg and H. S. Leff, J. Phys. A **22**, 4019 (1989).
[27] A. DeVos, J. Phys. Chem. **95**, 4534 (1991).