

Power and efficiency limits for internal combustion engines via methods of finite-time thermodynamics

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Analytical expressions for the upper bounds of power and efficiency of an internal combustion engine are obtained taking into account finite rate of heat exchange with the environment and nonzero entropy production due to chemical reactions. Recommendations of theoretically possible ways of improving internal combustion engines are presented.

I. INTRODUCTION

"In selecting an idealized process one is always faced with the fact that the simpler the assumptions, the easier the analysis, but the farther the result from reality" (Ref. 1, p. 23). The more assumptions we make, the farther we are likely to be from reality. On the other hand, detailed, realistic models for internal combustion engines are difficult and expensive to compute and analyze.² If we are interested in maximum power output or in maximum efficiency of internal combustion engines two ways of approaching the problem are possible. We could incorporate the major loss terms such as friction loss, heat leak, and incomplete combustion in a simple model based on air-standard cycle with rate-dependent loss mechanisms. Then using optimal control theory we can compute the piston trajectory which yields maximum power output. This approach has been realized in Refs. 3 and 4 and it is an application of the methods of finite-time thermodynamics. Another approach is to use a more detailed, "realistic" model and try only to find approximate upper limits for possible performance rather than to determine directly the optimum trajectory which yields the best performance. This approach has been realized in Ref. 5 and it is also an application of the methods of finite-time thermodynamics.

Estimates in Ref. 5 were obtained with the help of energy and entropy balances, which follow from the equations for a detailed model and its boundary conditions. In the analysis of minimal heat consumption for heat-driven separation processes,⁶ balances of energy, entropy, and material were also used to get estimates, but these forms of balances were postulated rather than deduced from a detailed model. In this work we use the same approach: we postulate the forms of energy, entropy, and material balances. These balances are valid for many detailed models and they are the only information that is used in order to get analytical expressions for maximum power and maximum efficiency. A new step taken in this work beyond Refs. 5 and 6 is the estimation of the average internal entropy production due to chemical reactions in order to get more precise upper limits for power and efficiency. The first attempt to analyze a chemically driven engine from

the viewpoint of finite-time thermodynamics was made in Ref. 7, where the authors used such strong assumptions as temperature independence of reaction rates and quick equilibration of hydrodynamic degrees of freedom. In this work we are not using these assumptions.

An unusual conclusion is derived from estimates we obtain for power and efficiency: in order to produce maximum power an internal combustion engine must have an input of heat from the environment. Thus, cooling systems in some cases reduce the maximum power of the engine. The same is true for the efficiency: the most efficient (within some range of the parameters) internal combustion engines should be built with heating systems rather than cooling systems. Of course, there are technological limits caused by strength and durability of the material, but it is possible to overcome these limits in the future. In this article, principal thermodynamic limits are obtained, which could not be overcome with any technology. And in order to be close to these limits we have to heat the engine, not cool it.

II. BALANCES OF ENERGY AND ENTROPY FOR THE ENGINE

For simplicity we shall consider a process in a one-cylinder internal combustion engine. Such process is shown schematically in Fig. 1.

Under the assumptions of negligible potential and kinetic energy of flows J_{inl} and J_{out} , and of Newtonian heat transfer through the walls of the cylinder and through the piston, the energy balance for the mixture inside the cylinder has the form

$$\frac{dE}{dt} = J_{\text{inl}} h_{\text{inl}} - J_{\text{out}} h_{\text{out}} - \int_{A(t)} \alpha (T - T_0) da - \mathcal{P}(t). \quad (1)$$

Here $E(t)$ is a total energy of the system, J_{inl} and J_{out} are mass flows of fuel-air mixture and exhaust gases; correspondingly, h_{inl} and h_{out} are specific enthalpies of the flows, $\alpha = \alpha(\xi)$ is a heat transfer coefficient between the inner surface of the cylinder or piston and the environment, $T_0(t, \xi)$ is the temperature of the thermal boundary layer of the environment (Ref. 7, p. 10), \mathcal{P} is the indicated power (Ref. 1, p. 9) (the power which is delivered as the work done on a piston), $T = T(t, \xi)$ is the temperature of

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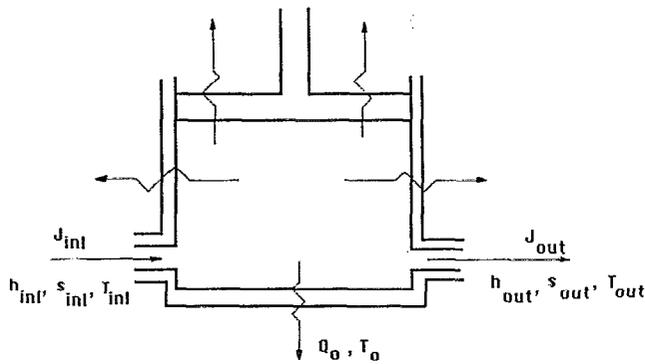


FIG. 1. Schematic representation of the engine with inputs on the left, outflow on the right, the piston at the top, and heat leakage through all the walls.

the fuel-air mixture and $\xi = (\xi_1, \xi_2, \xi_3)$ is a vector of coordinates of a point in some Cartesian system; integration in (1) is carried out over the area of the surface $A(t)$, which is the inner boundary of the cylinder and the piston.

Remark 1. The assumption of Newtonian heat transfer on the boundary is usually made in analysis of the internal combustion engine (Ref. 1, p. 266). For cylinder walls and cooling (heating) systems with complicated geometry, heat losses (gains) could be calculated by solving the heat conduction equation⁸ for the engine's walls and by using the Newtonian heat transfer law on the outer surfaces of the engine.

The entropy balance has the form

$$\frac{dS}{dt} = J_{inl}s_{inl} - J_{outl}s_{outl} - \int_{A(t)} \frac{\alpha(T - T_0)}{T} da + \sigma(t), \quad (2)$$

where $S(t)$ is the total entropy of the fuel-air mixture in the cylinder, and $\sigma(t) \geq 0$ is the total entropy production inside the system.

The process in the cylinder is periodic. From periodicity it follows that $E(0) = E(\tau)$, $S(0) = S(\tau)$, and $M(0) = M(\tau)$. Here $M(\tau)$ is the total mass of the working fluid and time τ is the period. These conditions were called, in Refs. 5 and 6, weak periodicity. In our analysis we shall use these integral conditions, balances, and the entropy production due to chemical reactions (one of the non-negative terms in the total entropy production).

The inlet fuel-air mixture is not in local equilibrium with respect to densities of all possible chemical species, because the engine is driven by exothermic chemical reactions. The exhaust gases may also be locally out of equilibrium with respect to the molar densities of the species because relaxation times for the reactions in the cylinder may be greater than the period τ . Thus, the problem arises of how to calculate s_{inl} and s_{outl} . We adopt the following procedure: assuming that the entropy densities of pure components of each inlet species $s_{inl}^i(T_{inl}, n_{inl}^i)$, $i = 1, \dots, k$, are known we simply add them and divide by mass density in order to get s_{inl} . Thus

$$s_{inl} = \sum_{i=1}^k s_{inl}^i(T_{inl}, n_{inl}^i) / \rho_{inl},$$

where n_{inl}^i is the molal density of the i th pure component, and ρ_{inl} is the density of the inlet fuel-air mixture. The same procedure is proposed for the calculation of s_{outl} . If we know specific entropies of fuel and air separately and if they have the same temperature, then

$$s_{inl} = s_{inl}^{air} / (F + 1) + s_{inl}^{fuel} F / (F + 1),$$

where F is the fuel-air ratio (Ref. 1, p. 68), $F = J_{inl}^{fuel} / J_{inl}^{air}$, J_{inl}^{fuel} is the inlet fuel mass flow, J_{inl}^{air} is the inlet air mass flow, and $J_{inl} = J_{inl}^{fuel} + J_{inl}^{air}$.

Let us now calculate the maximum average power (maximum power per cycle) \mathcal{P}_{max} of a weakly periodic process using (1) and (2) and assuming that T_0 is constant. From (1) it follows that

$$\bar{\mathcal{P}} = -\bar{f}_h - Q_0, \quad (3)$$

where $\bar{f}_h = (1/\tau) \int_0^\tau f_h(t) dt$,

$$f_h(t) = J_{out}(t)h_{out} - J_{inl}(t)h_{inl},$$

and

$$Q_0 = \frac{1}{\tau} \int_0^\tau \int_{A(t)} \alpha(T - T_0) da dt$$

is the average heat flow out of the engine into the environment. For engines with cooling systems, $Q_0 > 0$. From (3) it follows

$$\bar{\mathcal{P}} \leq -\bar{f}_h. \quad (4)$$

From entropy balance (2) we have

$$\bar{f}_s + \delta = -Q_0/T_0, \quad (5)$$

where

$$f_s(t) = J_{out}(t)s_{out} - J_{inl}(t)s_{inl}$$

and

$$\delta = -\frac{1}{\tau} \int_0^\tau \left[\sigma(t) + \int_{A(t)} \alpha(T - T_0) \left(\frac{1}{T_0} - \frac{1}{T} \right) da \right] dt.$$

It is easy to see that $\delta < 0$ with equality holding for a reversible process. From (3) and (5) it follows that

$$\bar{\mathcal{P}} = -\bar{f}_h + T_0 \bar{f}_s + T_0 \delta. \quad (6)$$

From the equality (6) and the inequality $\delta < 0$ we get

$$\bar{\mathcal{P}} \leq \mathcal{P}_{max} = T_0 \bar{f}_s - \bar{f}_h. \quad (7)$$

Let us now compare inequalities (7) and (4). From periodicity of total mass it follows that $\bar{J}_{out} = \bar{J}_{inl}$. From the fact that the entropy is growing in the chemical reactions, so that $s_{out} > s_{inl}$, it is reasonable to assume $\bar{f}_s > 0$. From $\bar{f}_s > 0$, it follows that the general power limit \mathcal{P}_{max} is greater than the power limit (4). The conclusion is that the engines without the restriction $Q_0 > 0$ theoretically could produce greater power. Thus, it could be better to construct engines with heating systems rather than cooling systems.

Remark 2. When $T_0 = T_{inl} = T_{out}$, from (7) it follows that

$$\begin{aligned} \mathcal{P}_{\max} &= (h_{inl} - T_0 s_{inl}) \bar{J}_{inl} - (h_{out} - T_0 s_{out}) \bar{J}_{out} \\ &= (g_{inl} - g_{out}) \bar{J}_{inl}, \end{aligned}$$

where g is a specific Gibbs free energy.

Let us define the efficiency of an internal combustion engine as

$$\eta = \frac{\bar{\mathcal{P}}}{-\bar{f}_h}. \quad (8)$$

Several definitions of efficiency are discussed in Ref. 1, p. 9. Our definition (8) is close to the "indicated thermal efficiency" of Ref. 1. From (6) we obtain

$$\eta = 1 + \frac{T_0 \bar{f}_s}{-\bar{f}_h} + \frac{T_0 \delta}{-\bar{f}_h}. \quad (9)$$

If $-\bar{f}_h > 0$, then from (9),

$$\eta < \eta_{\max} = 1 + \frac{T_0 \bar{f}_s}{-\bar{f}_h} = 1 + T_0 \frac{s_{out} - s_{inl}}{h_{inl} - h_{out}}. \quad (10)$$

Remark 3. When $h_{inl} > h_{out}$ and $s_{inl} < s_{out}$ we have $\eta_{\max} > 1$. We get a paradoxical conclusion, contradicting the general notion that efficiency is less than 1, because we have used, instead of the standard air cycle efficiency (Ref. 1, p. 32), another efficiency definition, which allows an unconventional account of heat input, especially if the heat input itself is unconventional.

Finite-rate heat exchange with the environment and internal entropy production impose new limits on power and efficiency of internal combustion engines. We present in the next section analytical expressions for these new upper bounds of performance. They are obtained with the same mathematical technique, as the results of Refs. 5 and 6.

III. BEST PERFORMANCE FOR FINITE-RATE HEAT EXCHANGE

Average power is connected with heat exchange by the formula (3). In this section the temperature of the environment $T_0(t, \xi)$ is a given function of time and space variables. In order to find an upper limit of power we add the constraint $S(0) = S(\tau)$, with its Lagrange multiplier λ , to the right-hand side of (3). As a result we get the equality

$$\begin{aligned} \bar{\mathcal{P}} &= -\bar{f}_h + \frac{1}{\tau} \int_0^\tau \int_{A(t)} \alpha(T_0 - T) \left(1 + \frac{\lambda}{T} \right) da dt \\ &\quad + \lambda (\bar{\sigma} - \bar{f}_s). \end{aligned} \quad (11)$$

Using the temperature of fuel-air mixture $T(t, \xi)$ as a control and minimizing (11) over $T(t, \xi) > 0$ with fixed $\lambda < 0$, we get

$$\bar{\mathcal{P}} < -\bar{f}_h + \lambda (\bar{\sigma} - \bar{f}_s) + \frac{1}{\tau} \int_0^\tau \int_{A(t)} \alpha (\sqrt{T_0} - \sqrt{-\lambda})^2 da dt. \quad (12)$$

Inequality (12) is true for all $\lambda < 0$. In order to get the best estimate we minimize the right-hand side of (12) with respect to λ . The optimum $\hat{\lambda}$ is given by

$$\sqrt{-\hat{\lambda}} = \beta / (\bar{f}_s + \gamma - \bar{\sigma}), \quad (13)$$

where

$$\beta = \frac{1}{\tau} \int_0^\tau \int_{A(t)} \alpha(\xi) \sqrt{T_0(t, \xi)} da dt,$$

and

$$\gamma = \frac{1}{\tau} \int_0^\tau \int_{A(t)} \alpha(\xi) da dt.$$

Remark 4. Minimization with respect to $\lambda < 0$ of the right-hand side of (12) gives a finite value only if $\bar{\sigma} < \bar{f}_s + \gamma$; otherwise we get $-\infty$. This implies that the inequality $\bar{\sigma} < \bar{f}_s + \gamma$ is true for any weakly periodic process. Substituting (13) into (12) we get

$$\begin{aligned} \bar{\mathcal{P}} &< \hat{\mathcal{P}}_{\max}(\bar{\sigma}) \\ &= -\bar{f}_h - \frac{\beta^2}{\bar{f}_s + \gamma - \bar{\sigma}} + \frac{1}{\tau} \int_0^\tau \int_{A(t)} \alpha(\xi) T_0(t, \xi) da dt. \end{aligned} \quad (14)$$

$$\eta < \hat{\eta}_{\max}(\bar{\sigma}) = -\hat{\mathcal{P}}_{\max}(\bar{\sigma}) / \bar{f}_h.$$

When $T_0(t, \xi) = \text{const}$, from (14) it follows that

$$\hat{\mathcal{P}}_{\max}(\bar{\sigma}) = -\bar{f}_h + T_0 \gamma \frac{\bar{f}_s - \bar{\sigma}}{\bar{f}_s + \gamma - \bar{\sigma}}. \quad (15)$$

Function $\hat{\mathcal{P}}_{\max}$ from (14) is monotonically decreasing in the argument $\bar{\sigma}$, because

$$\frac{d\hat{\mathcal{P}}_{\max}}{d\bar{\sigma}} = -\frac{\beta^2}{(\bar{f}_s + \gamma - \bar{\sigma})^2} < 0. \quad (16)$$

That is why, in order to get an upper limit for power, we could use $\bar{\sigma} = 0$ in (14) or (15). A corresponding estimate for (15) is

$$\bar{\mathcal{P}} < -\bar{f}_h + T_0 \bar{f}_s \frac{\gamma}{\bar{f}_s + \gamma}. \quad (17)$$

Inequality (17) gives a more precise estimate of power than the corresponding reversible estimate (7). Using (17) we get the inequality for the efficiency:

$$\eta < \hat{\eta}_{\max}(0) = 1 + T_0 \frac{s_{out} - s_{inl}}{h_{inl} - h_{out}} \frac{\gamma}{\bar{f}_s + \gamma}. \quad (18)$$

Evaluating (16) at $\bar{\sigma} = a$ for $T_0(t, \xi) = \text{const}$, we have

$$\frac{d\hat{\mathcal{P}}_{\max}}{d\bar{\sigma}} = -\frac{\gamma^2 T_0}{(\bar{f}_s + \gamma - a)^2}. \quad (19)$$

Formula (19) gives us the explanation of why it is hard (but theoretically not impossible) to construct engines with efficiency (18): with the increase of the temperature T_0 the negative influence of internal entropy production on power output may grow. If for some constant $a > 0$ we get an estimate of average internal entropy production $\bar{\sigma} > a$,

then from (16) it follows that $\mathcal{P} \leq \hat{\mathcal{P}}_{\max}(a)$ and $\eta < \hat{\eta}_{\max}(a)$. From (19) we find that dependence on the internal entropy production is important in choosing the possible configuration of the engine. Indeed, when $a < \bar{f}_s$ the heating system may have a positive effect on power and efficiency, when $a > \bar{f}_s$ it is impossible to improve the engine by heating because it is forbidden by the entropy balance (2) and the periodicity condition $S(0) = S(\tau)$. Now it is clear why it is important to estimate internal average entropy production of the engine under consideration. In the next section we give the lower estimate of the internal average entropy production inside the cylinder due to the chemical reactions.

IV. CHEMICAL KINETICS AND INTERNAL ENTROPY PRODUCTION

We give here the lower bounds for the average internal entropy production due to chemical reactions in the engine under consideration. It is assumed that reactions are reversible and that the law of mass action (Ref. 9, p. 204), holds. For better understanding let us first consider the description of chemical reactions occurring uniformly in the space in an isolated constant-volume vessel. The corresponding equations are

$$\frac{de}{dt} = 0, \quad (20)$$

$$\frac{dn_j}{dt} = \sum_{i=1}^r \nu_{ij} J_i, \quad j = 1, \dots, k,$$

where e is the energy density, n_j is the molar density of j th component,

$$J_i = k_i^f(T) \prod_{j=1}^k n_j^{\alpha_{ij}} - k_i^r(T) \prod_{j=1}^k n_j^{\beta_{ij}},$$

$\nu_{ij} = \beta_{ij} - \alpha_{ij}$, α_{ij} and β_{ij} are the stoichiometric coefficients (Ref. 10, p. 23), and

$$K_i^c(T) = k_i^f(T) / k_i^r(T).$$

The equilibrium constant of the i th reaction $K_i^c(T)$ is connected with chemical potentials by the formula

$$K_i^c(T) = \exp\left(-\sum_{j=1}^k \mu_j^0(T) \nu_{ij} / (RT)\right),$$

where

$$\mu_j = RT \ln(n_j) + \mu_j^0(T)$$

is the chemical potential of the j th component. Equation system (20) will be closed if we express temperature T as a function of energy density e and component molar densities n_j . To realize this it is assumed that entropy density $s(e, n_1, \dots, n_k)$ is known. Then

$$T(e, n_1, \dots, n_k) = 1 / \frac{\partial s(e, n_1, \dots, n_k)}{\partial e}.$$

Note that $s(e, n_1, \dots, n_k)$ does not correspond to equilibrium with respect to molar densities n_1, \dots, n_k . Indeed, we shall show that this function is growing along the trajectory of

(20). We propose to calculate $s(e, n_1, \dots, n_k)$ in the same way as s_{inl} and s_{out} were calculated in Sec. II. The only difference is that here we need a state function. That is why we use the formula

$$s(e, n_1, \dots, n_k) = \max_{\sum e_i = e} \sum_{i=1}^k s^i(e_i, n_i), \quad (21)$$

where e_i is the energy density, n_i is the molar density, and s^i is the entropy density of the i th pure component.

Differentiating (21) at the solution of (20) we get the entropy production

$$\frac{ds}{dt} = \sigma_{\text{ch}} = \frac{\partial s}{\partial e} \frac{de}{dt} + \sum_{j=1}^k \frac{\partial s}{\partial n_j} \frac{dn_j}{dt} = \sum_{i=1}^r -\frac{A_i J_i}{T}, \quad (22)$$

where $A_i = \sum_{j=1}^k \mu_j \nu_{ij}$ is the affinity of i th reaction (Ref. 9, p. 206). The rate of the i th reaction J_i may be expressed with the help of affinities in the following way:

$$J_i = k_i^f(T) \prod_{j=1}^k n_j^{\alpha_{ij}} \left[1 - \exp\left(\frac{A_i}{RT}\right)\right]. \quad (23)$$

From (22) and (23) we find $\sigma_{\text{ch}} \geq 0$. Indeed,

$$\sigma_{\text{ch}} = R \sum_{i=1}^r k_i^f(T) \prod_{j=1}^k n_j^{\alpha_{ij}} \left[\exp\left(\frac{A_i}{RT}\right) - 1\right] \frac{A_i}{RT} \geq 0 \quad (24)$$

because $[\exp(x) - 1]x \geq 0$ for all x .

We now formulate the problem of estimating the chemical entropy production for the internal combustion engine under consideration. The material balances for the cylinder have the form

$$\frac{dN_j}{dt} = J_{\text{inl}} \frac{c_j^{\text{inl}}}{M_j} - J_{\text{out}} \frac{c_j^{\text{out}}}{M_j} + \int_{\Omega(t)} \left(\sum_{i=1}^r \nu_{ij} J_i\right) d\xi, \quad j = 1, \dots, k, \quad (25)$$

where

$$N_j(t) = \int_{\Omega(t)} n_j(t, \xi) d\xi$$

is the total molar amount of component j in the cylinder,

$$c_j = M_j n_j / \left(\sum_{j=1}^k M_j n_j\right)$$

is the mass fraction of j th component, and M_j is the molar mass of j th component. Integration is carried out over the volume of the cylinder. Averaged over the cycle time τ entropy production due to chemical reactions has the form (Ref. 9, p. 26)

$$\bar{\sigma}_{\text{ch}} = \frac{1}{\tau} \int_0^\tau \int_{\Omega(t)} \sum_{i=1}^r -\frac{A_i J_i}{T} d\xi dt. \quad (26)$$

It is obvious that $\bar{\sigma}$ from (15) is greater than or equal to $\bar{\sigma}_{\text{ch}}$; thus, from $\bar{\sigma}_{\text{ch}} \geq a$ follows $\bar{\sigma} \geq a$. Our problem now is to find a lower bound of (26) using the periodicity constraints $N_j(0) = N_j(\tau)$, $j = 1, \dots, k$. With the notation

$$\bar{F} = \frac{1}{\tau} \int_0^\tau \frac{dt}{V(t)} \int_{\Omega(t)} F(t, \xi) d\xi$$

we can get the equivalent formulation of this problem: to find positive lower bound of

$$-V(t) \sum_{i=1}^r \frac{A_i J_i}{T} \quad (27)$$

with constraints

$$V(t) \sum_{i=1}^r \nu_{ij} J_i = y_j, \quad j=1, \dots, k, \quad (28)$$

where

$$y_j = \frac{1}{\tau} \int_0^\tau \left(J_{\text{out}}(t) \frac{c_j^{\text{out}}}{M_j} - J_{\text{in}}(t) \frac{c_j^{\text{in}}}{M_j} \right) dt,$$

and $V(t) = \int_{\Omega(t)} d\xi$ is the volume on the cylinder.

We are solving averaged optimization problems (27) and (28) using the hierarchical method that combines Lagrange multipliers with successive constraint breaking. This method was first used for spatially uniform finite-time thermodynamics problems in Ref. 11, evolving from the work of Rozonoer and Tsirlin and Tsirlin.^{12,13} Its power was expanded to treat considerably more complicated non-uniform problems in Refs. 5 and 6. In (27), (28), and (23), temperature, molar densities of the components, and affinities are functions of time and space variables and volume is a function of time. These functions are connected with each other through the detailed, case-specific model. In order to get estimates we could break these inner constraints and consider $T > 0$, $n_j > 0$, $j=1, \dots, k$, A_i , $i=1, \dots, r$, $V_{\min} < V(t) < V_{\max}$ as controls. But the more realistic physical restrictions we impose on controls the better estimation we shall get. This is why we express the rates of the reactions in the form

$$J_i = k_i^f(T) \exp\left(\frac{-\sum_{j=1}^k \mu_j^0(T) \alpha_{ij}}{RT}\right) \left[\exp\left(\frac{A_i^f}{RT}\right) - \exp\left(\frac{A_i^r}{RT}\right) \right] \quad (29)$$

instead of the conventional form (23). Here $A_i^f = \sum_{j=1}^k \mu_j \alpha_{ij}$ and $A_i^r = \sum_{j=1}^k \mu_j \beta_{ij}$. Now we are able to choose another set of controls $T > 0$, $B_i^f = A_i^f/RT$, $B_i^r = A_i^r/RT$, $i=1, \dots, r$, $V_{\min} < V(t) < V_{\max}$. Additional physical restrictions on these controls are $B_i^f < 0$, $B_i^r < 0$, which follow from $T > 0$, $\mu_j < 0$, $j=1, \dots, k$, $\alpha_{ij} > 0$, $\beta_{ij} > 0$. These restrictions are true for any detailed model. With the notation

$$k_i^*(T) = R k_i^f(T) \exp\left(-\sum_{j=1}^k \mu_j^0(T) \alpha_{ij} / (RT)\right)$$

our problem is to find a positive lower bound for

$$V \sum_{i=1}^r k_i^*(T) (B_i^f - B_i^r) [\exp(B_i^f) - \exp(B_i^r)] \quad (30)$$

with constraints

$$V \sum_{i=1}^r \nu_{ij} k_i^*(T) [\exp(B_i^f) - \exp(B_i^r)] = R y_j, \quad j=1, \dots, k, \quad (31)$$

and controls $V_{\min} < V(t) < V_{\max}$, $T(t, \xi) > 0$, $B_i^f(t, \xi) < 0$, $B_i^r(t, \xi) < 0$, and $i=1, \dots, r$.

Let us first consider one reaction including k species. In this case $r=1$. With notations $k_1^{\max} = \max_{T>0} k_1^*(T)$ and

$$y_1^* = R \sum_{j=1}^k \nu_{1j} y_j / \left(\sum_{j=1}^k \nu_{1j}^2 \right),$$

the problem of (30) and (31) is equivalent to the minimization of

$$V k_1^* T (B_1^f - B_1^r) [\exp(B_1^f) - \exp(B_1^r)]$$

with constraint

$$V k_1^*(T) [\exp(B_1^f) - \exp(B_1^r)] = y_1^*.$$

We assume that $k_1^{\max} < +\infty$. Then, using Lagrange multipliers, we get the lower-bound estimate

$$\begin{aligned} \bar{\sigma}_{\text{ch}} > \min_{B_1^f < 0, B_1^r < 0} \{ V^{\max} k_1^{\max} [\exp(B_1^f) - \exp(B_1^r)] \\ \times (B_1^f - B_1^r + \lambda) - \lambda y_1^* \}. \end{aligned} \quad (32)$$

Maximizing the right-hand side of (32) with respect to λ we get the greatest lower bound. The result is

$$\bar{\sigma}_{\text{ch}} > -|y_1^*| \ln \left(1 - \frac{|y_1^*|}{V^{\max} k_1^{\max}} \right). \quad (33)$$

Remark 5. If $|y_1^*| \geq V^{\max} k_1^{\max}$, maximization with respect to λ in (32) gives $+\infty$. This implies that inequality $|y_1^*| < V^{\max} k_1^{\max}$ is true for any solution of a detailed model.

For r linearly independent chemical reactions the result is similar. We use the notations $k_i^{\max} = \max_{T>0} k_i^*(T)$, $i=1, \dots, r$, $C_{il} = \sum_{j=1}^k \nu_{ij} \nu_{lj}$, $i, l=1, \dots, r$ and

$$y_i^* = R \sum_{l=1}^r C_{il}^{-1} \sum_{j=1}^k \nu_{lj} y_j, \quad i=1, \dots, r,$$

where

$$\sum_{l=1}^r C_{il} C_{lj}^{-1} = \delta_{ij},$$

$\delta_{ij} = 1$ when $i=j$, $\delta_{ij} = 0$ when $i \neq j$. We carry out the same minimization with respect to $B_i^f < 0$ and $B_i^r < 0$ and maximization with respect to λ , as previously, and get

$$\bar{\sigma}_{\text{ch}} > - \sum_{i=1}^r |y_i^*| \ln \left(1 - \frac{|y_i^*|}{V^{\max} k_i^{\max}} \right). \quad (34)$$

Inequality (34) is obtained using assumptions $k_i^{\max} < +\infty$, $i=1, \dots, r$. If for some reaction i_0 we have $k_{i_0}^{\max} = +\infty$, the corresponding term in (34) is equal to zero; thus, we could extend the formula (34) to this situation also.

Remark 6. If $|y_i^*| \geq V^{\max} k_i^{\max}$ for some i , maximization with respect to λ gives $+\infty$. This implies that inequalities $|y_i^*| < V^{\max} k_i^{\max}$, $i=1, \dots, r$ are true for any solution of a detailed model.

The situation of linearly dependent chemical reactions could be analyzed using methods of nonlinear optimization. First, with the help of Lagrange multipliers, we construct the function

$$a = \min_{B_i^f, B_i^r < 0} \left[\sum_{i=1}^r V_i^{\max} k_i^{\max} [\exp(B_i^f) - \exp(B_i^r)] \right. \\ \left. \times \left(B_i^f - B_i^r + \sum_{j=1}^k \lambda_j \nu_{ij} \right) \right] - R \sum_{j=1}^k y_j \lambda_j.$$

One can show that

$$a(\lambda_1, \dots, \lambda_k) = \sum_{i=1}^r k_i^{\max} V_i^{\max} \psi \left(\left| \sum_{j=1}^k \lambda_j \nu_{ij} \right| \right) \\ - R \sum_{j=1}^k y_j \lambda_j, \quad (35)$$

where

$$\psi(y) = 1 - y - x(y) - \exp[x(y)], \quad x(y) = f^{-1}(y),$$

$$y = f(x) = \exp(-x) - x - 1,$$

and

$$x[f(x)] = x.$$

As soon as we compute $a(\lambda_1, \dots, \lambda_k)$ for given $\lambda_1, \dots, \lambda_k$, we have an estimate $\bar{\sigma}_{ch} \geq a$. The best estimate could be found by maximizing (35) with respect to $\lambda_1, \dots, \lambda_k$.

V. CONCLUSIONS

Theoretical results of this paper may be useful in two different ways. First, it is more realistic to compare power and efficiency of real engines to (14) than to air-standard

cycle efficiency. Second, it may be a stimulus for research in the field of constructing highly efficient nonconventional internal combustion engines with heating systems instead of cooling systems.

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