

Probabilistic Finite Time Thermodynamics: A Chemically Driven Engine

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Abstract

The methods of finite-time thermodynamics are complemented with some probabilistic concepts allowing a more accurate description of the performance indicators of a power system. A chemical reaction is studied. The model is a flow reactor coupled by a heat exchanger to an engine. The probabilistic approach put into evidence the existence of a maximum flow rate in the reactor which, when exceeded, with some probability does not allow the reaction to start and, consequently, the power to be generated. The power fluctuations depend on the initial concentration of the fuel, i.e. on its quality. The model is also appropriate for solid fuels. All the statistical indicators show that there is a finite flow rate that yields maximum engine power, and that the maximum fuel efficiency is always attained at the uninteresting limit of zero flow rate.

1. Introduction

The field of finite-time thermodynamics was started in 1975 as a result of the increased awareness of the limitations of the Earth's resources. The oil crisis of 1973 made it clear that energy sources are neither inexhaustible nor free. The criteria of merit provided by traditional reversible thermodynamics were, with few exceptions, far too unrealistic for evaluating the potential for conservation in real processes. Irreversible thermodynamics could in principle evaluate the losses in rate processes, but it requires extensive knowledge of the microscopic mechanism of the process, something which is usually not available and which relies on rather severe assumptions far from equilibrium. These observations prompted some researchers to formulate a macroscopic theory of loss processes in the tradition of reversible thermodynamics and requiring as little additional information about the system as possible. This theory is known as finite-time thermodynamics (for a good early review see [1]; new results are reviewed in [2, 3]).

From common practice we know, however, that by decreasing the duration allowed for any given process there is a threshold under which the probability that the process really occurs becomes significantly different from zero or unity. This is of course of no importance in traditional reversible thermodynamics, where the duration allowed to the process is infinite and, consequently, the process surely occurs. The situation is drastically changed in finite-time thermodynamics, where the finiteness of the process duration is essential. Another kind of limitation characterizes obviously the finite resources. It refers to their quality. It is well known for example that poor solid fuels have significant fluctuations of the caloric power. Are these fluctuations intrinsic or could they arise from the combustion process? This question requires also a statistical and/or probabilistic analysis. A third situation when the limitation is essential refers to those processes which occur in systems with small spatial extension, where the total number of particles is reduced. The recent interest in such small systems is an indirect consequence of the finite Earth resources. As examples we quote processes occurring in genetic engineering and microelectronics. In all these cases the use of intensive quantities is sometimes of little help because of the breakdown on the laws of large numbers. The implications of finite resources were first treated in [4, 5] while the effect of small size has been developed extensively in [6], although still in a macroscopic fashion.

In this paper we prove that probability concepts can significantly improve the performance of the usual finite-time thermodynamic methods. The cost of this improvement is on one hand the necessity to add to the macroscopic thermodynamic model some microscopic details and, on the other hand, the need for more elaborate mathematical techniques.

The simple system adopted here for illustration is a continuous flow tube reactor that converts reactants to products in an exothermic process and thus supplies heat to an engine. The time constraints enter through the rate coefficients of the chemical reactions. The simplifying assumption is made that the rate coefficients are independent of temperature. This provides a simple model of the boiler section of a power plant. The reaction supplying heat will not, in general, go to completion, and the temperature of the heat delivered to the engine may be lower than that of the reactor. This system was studied in [7], while in [8] the assumption of temperature independent rate coefficients was relaxed. In both quoted papers the treatment was based on usual finite-time thermodynamic methods. Here we shall show that more detailed quantitative and even qualitative conclusions can be reached when probabilistic methods are added.

In the next section we review the model of a chemically driven engine first proposed in [7] (for conceptual details see the quoted paper). In subsequent sections the model is analyzed by using probabilistic concepts for commonly encountered systems following first order kinetics. All the three restrictions previously mentioned (namely, duration, quality and number of particles) will be discussed.

2. Model of a chemically driven engine

Consider the exothermic process $R \rightarrow P$ which releases an amount of heat per unit time q_r . Suppose that this process supplies its heat to a heat engine. $T(f)$ is the "flame"

temperature at which q_r is released from the chemical reaction, and T_2 is the temperature of the hot reservoir of the engine. Suppose further that the chemical reaction occurs in a flow tube (length l and cross sectional area A). Let us denote by f the fuel flow rate at the reactor inlet, measured in number of particles per unit time. The same fuel flow rate measured in unit volume per unit time will be denoted \dot{V}_f . The two quantities are related through $f = \dot{V}_f R'_0$ where R'_0 is the initial reactant (fuel) concentration. We define the dwell (or traversal) time τ as the ratio $\tau = (Al)/\dot{V}_f$. τ is the time during which the reaction is allowed to proceed. The mean fuel velocity at the reactor inlet is denoted $v_f (\equiv l/\tau)$. The extent of the reaction $\varepsilon(\tau)$ is defined as

$$\varepsilon(\tau) = P'(\tau)/R'_0 \quad (1)$$

where P' is the product concentration. We may express q_r as

$$q_r = Q_p \varepsilon(\tau) f \quad (2)$$

where Q_p is the exothermicity of the reaction (in energy units per particle of reactant). Note that τ and f may be expressed in terms of each other, and q_r may be written as a function of the flow rate:

$$f = \frac{ALR'_0}{\tau}, \quad q_r(f) = Q_p f \varepsilon(f) \quad (3)$$

The functional dependence $\varepsilon(f)$ on f must be determined by the reaction kinetics.

Two cases of converting the reaction heat into work were considered in [7]:

Case I

The reaction heat q_r is extracted from the products emerging at the flame temperature $T(f)$ so that $T(f)$ is the highest temperature at which heat is supplied to do work. The finite heat capacity C of the reaction mixture was considered constant through the temperature range T_0 (the inlet temperature) to $T(f)$ (the flame temperature). The following relationship applies:

$$T(f) = T_0 + Q_p \varepsilon(f)/C \quad (4)$$

and the power production is given by

$$W(f) = Q_p f \varepsilon(f) - C T_0 f \ln \left[\frac{Q_p \varepsilon(f)}{C T_0} + 1 \right] \quad (5)$$

so long as the engine converts the heat of reaction into work with the maximum efficiency.

Case II

Another way in which a chemical process might drive a thermal engine would have the product mixture transfer heat to the high temperature reservoir of the thermal engine,

maintaining its temperature at T_H as in a steam generator. The product mixture escapes at T_H , carrying with it some of the energy produced by the combustion process. In this case T_H is independent of the flow rate and is presumably fixed by external factors. Then the rate of heat input to the engine q_H is

$$-q_H = fQ_p \varepsilon(f) - f \int_{T_0}^{T_H} C(T) dT \quad (6)$$

while the output power is

$$W = |q_H| \eta_{\text{engine}} \quad (7)$$

where η_{engine} is the engine efficiency, which need not be of Carnot type. The equation (6) is valid under the assumption that the heat capacity of the mixture $C(T)$ is roughly the same for reactants and products. When C is not dependent on temperature we find

$$-q_H = fQ_p \varepsilon(f) - fC(T_H - T_0) \quad (8)$$

This relationship will be used in the following.

3. Reversible first order kinetics

Consider the first order reaction



where R and P are the reactant and product, respectively. We denote by k_f and k_b the direct and reverse transition probabilities per unit time. We assume both k_f and k_b to be independent of temperature. This limitation makes the probabilistic model more tractable from a mathematical point of view.

We choose now a control volume V whose size should allow a stochastic description wherein the variables are the number of particles within the control volume, independently of their momenta or their internal states [9, p. 285]. The appropriate size of V depends, of course, on system and process. As an example, in case of reacting fluids it is of the order of the cube of a few mean free paths [9, p 288]. The control volume moves from the inlet towards the outlet of the reactor with constant velocity, reaching the end of the reaction tube after the dwell time τ . At the reactor inlet (time $t = 0$) the volume V contains only reactant (fuel) at concentration R'_0 . Then, the initial total number of reactant particles in the volume V is $R_0 \equiv VR'_0$. After the time t ($\leq \tau$) the control volume contains a mixture of fuel and products of reaction. Their concentrations are denoted $R'(t)$ and $P'(t) = R'_0 - R'(t)$ while the total number of reactant and product particles in the volume V is $R \equiv VR'$ and $P \equiv VP'$, respectively.

We denote by $\pi(P, t)$ the probability that at time t the control volume contains P particles of reaction product. At a subsequent moment this probability could change. We denote by $w(P_1, P_2)$ the transition probability from state (P_1) into state (P_2).

The reaction occurring in the control volume can be modeled as a Markov process. The assumption of a one-particle reaction (first order kinetics) allows to describe the time evolution of the system as a birth- and death-process. When the system is in the state (P), only the states ($P-1$) and ($P+1$) are accessible in the next time step. The appropriate master equations are [10, p.87]

$$\begin{aligned} \frac{d\pi(P, t)}{dt} = & w(P-1, P)\pi(P-1, t) - [(w(P, P-1) + w(P, P+1))\pi(P, t) \\ & + w(P+1, P)\pi(P+1, t)] \quad P = 1, 2, \dots, R_0 \end{aligned} \quad (10)$$

$$\frac{d\pi(0, t)}{dt} = w(1, 0)\pi(1, t) - w(0, 1)\pi(0, t) \quad P = 0 \quad (11)$$

The first order reaction (9) allows one to write, after a simple renormalization, the birth and death transition probabilities $w(P, P+1)$ and $w(P, P-1)$, respectively, as

$$w(P, P+1) = k_f R = k_f (R_0 - P) \quad w(P, P-1) = k_b P \quad (12)$$

By using eqns. (12) we can obtain another form of the master equations (10) and (11):

$$\begin{aligned} \frac{d\pi(P, t)}{dt} = & k_f [R_0 - (P-1)]\pi(P-1, t) - [k_f (R_0 - P) + k_b P]\pi(P, t) \\ & + k_b (P+1)\pi(P+1, t) \quad P = 1, 2, \dots, R_0 \end{aligned} \quad (13)$$

$$\frac{d\pi(0, t)}{dt} = k_b \pi(1, t) - k_f R_0 \pi(0, t). \quad (14)$$

The following initial conditions have to be used:

$$\begin{aligned} \pi(P, 0) = & 1 \quad P = 0 \\ & 0 \quad P \neq 0 \end{aligned} \quad (15)$$

i.e. at time $t = 0$ (at the reactor inlet) surely there is no single product particle.

Equations (13) and (14) are finite-difference equations with linear coefficients. The finite-difference property is a result of the discreteness of the stochastic variable – the number of product particles in the control volume – while the linearity of the coefficients is a consequence of the one-particle character (first order kinetics) of the reaction (9). The role of the limitation of the present analysis to first order reaction becomes now evident. Indeed, in this case an analytical solution for the eqs. (13) – (15) can be found. When higher order reactions are considered, solving the master equations associated with them is a difficult task which requires further investigations.

The solution of eqns. (13) – (15) is (see Appendix):

$$\pi(P, t) = C_{R_0}^P \left[\frac{k_f}{k_f + k_b} e^{-(k_f + k_b)t} \right]^{R_0} [e^{(k_f + k_b)t} - 1]^P \left[\frac{k_b}{k_f} e^{(k_f + k_b)t} + 1 \right]^{R_0 - P}$$

$$P = 0, 1, \dots, R_0 \quad (16)$$

By using eq. (16) we can determine the mean value of the reaction extent $\varepsilon_{\text{mean}}$ which is given by $\varepsilon_{\text{mean}} = P'_{\text{mean}}/R'_0 = P_{\text{mean}}/R_0$ (see Appendix):

$$\varepsilon_{\text{mean}} = \frac{1}{r + 1} [1 - e^{-(1+r)k_f t}] \quad (17)$$

where $r = k_b/k_f$. This expression was previously derived in [7] by using the rate equations method. It is obvious, however, that the probabilistic approach amplifies the information we could obtain by using classical methods. Indeed, from eq. (16) we learn that for a given time the reaction extent $\varepsilon = P'/R'_0 = P/R_0$ could have values quite different from the mean value $\varepsilon_{\text{mean}}$ given by eq. (17), and, more than that, we can evaluate the probabilities of all these possible values.

The superiority of the probabilistic approach over the classical one is obvious when we try to understand and/or describe the fluctuations which usually are associated with the experimental data. The classical approach allows average values to be evaluated only. The probabilistic techniques make possible, however, the computation of higher order moments. To be more specific, new information concerning the time properties of the reaction mixture we study here can be obtained by computing the variance $D^2(P)$. This is a measure of the fluctuations of the number of product particles from the control volume around its mean value $P_{\text{mean}}(t) = R_0 \varepsilon_{\text{mean}}(t)$. After some algebra we obtain (see Appendix):

$$D^2(P(t)) = P_{\text{mean}}(t)(1 - \varepsilon_{\text{mean}}(t)). \quad (18)$$

We see that generally $D^2 \neq P_{\text{mean}}$. Consequently, the distribution $\pi(P, t)$ is not Poissonian and generally the fluctuations are not negligible compared to the average values. Also note that $D^2(P(0)) = 0$. This is not surprising because we accepted the initial number of product particles as being known. The large fluctuations at later times allow both extreme outcomes for any dwell time τ , namely the reaction does not start ($P(\tau) = 0$) and the fuel is completely consumed ($P(\tau) = R_0$), respectively. Indeed, eq. (16) shows that the probabilities of either of these cases are non-zero (but usually very small).

The standard deviation of the reaction extent $\sigma(\varepsilon)$ can be evaluated from the standard deviation of P , namely $\sigma(P) = [D^2(P)]^{1/2}$, and the definition $\sigma(\varepsilon) = \sigma(P)/R_0$. By using eq. (18) we obtain

$$\sigma(\varepsilon) = \frac{\sqrt{\varepsilon_{\text{mean}}(1 - \varepsilon_{\text{mean}})}}{\sqrt{R_0}} \quad (19)$$

The magnitude of $\sigma(\varepsilon)$ is a function of the initial number R_0 of reactant particles. We should remind that R_0 depends on both the control volume V and the initial reactant concentration R'_0 ($R_0 \equiv VR'_0$). In the limit of large R_0 $\sigma(\varepsilon)$ vanishes, and the fluctuations of the reaction extent are negligible. Consequently, the classical approach can be used successfully in this case. However, at smaller values of R_0 the standard deviation $\sigma(\varepsilon)$ is important (Fig. 1) and using probabilistic methods is recommended. Note that the fluctuations of the reaction extent are relatively more important at the beginning of the reaction, when ε is close to zero. Indeed, $\sigma(\varepsilon)/\varepsilon \sim (1/\varepsilon - 1)^{1/2} \rightarrow \infty$ when $\varepsilon \rightarrow 0$.

The actual time when the system changes from the state (P) into the state ($P + 1$) cannot be exactly known. However, an estimation of the moment when probably this event occurs can be made by using the approach we propose here. It is convenient to define this estimation (say $t_{P \rightarrow P+1}$) by assuming that when $t > t_{P \rightarrow P+1}$ the probability of the state ($P + 1$) exceeds that of the state (P). So, we can use $\pi(P, t_{P \rightarrow P+1}) = \pi(P + 1, t_{P \rightarrow P+1})$ to define $t_{P \rightarrow P+1}$. There is a numerable set of values $t_{P \rightarrow P+1}$ which correspond to $P = 0, \dots, R_0 - 1$.

The time when the reaction probably starts (say $t_{0 \rightarrow 1}$) can be defined through $\pi(0, t_{0 \rightarrow 1}) = \pi(1, t_{0 \rightarrow 1})$. By using this definition and eq. (16) we find:

$$t_{0 \rightarrow 1} = \frac{1}{(1+r)k_f} \ln \frac{R_0 + 1}{R_0 - r} \quad (20)$$

Equation (20) gives the minimum dwell time (probably) needed to start the reaction: $\tau_{\min} \equiv t_{0 \rightarrow 1}$. This minimum time can be correlated with a maximum flow rate f_{\max} . When $t < t_{0 \rightarrow 1}$ (i.e. $f > f_{\max}$) the reaction probably will not start. Note that $t_{0 \rightarrow 1} > 0$ even in case of no reverse reaction ($r = 0$). The minimum necessary dwell time increases by intensifying the reverse reaction (i.e. increasing r) and by diminishing the direct reaction (i.e. decreasing k_f). Both conditions characterize poor quality fuels. Generally, the initial

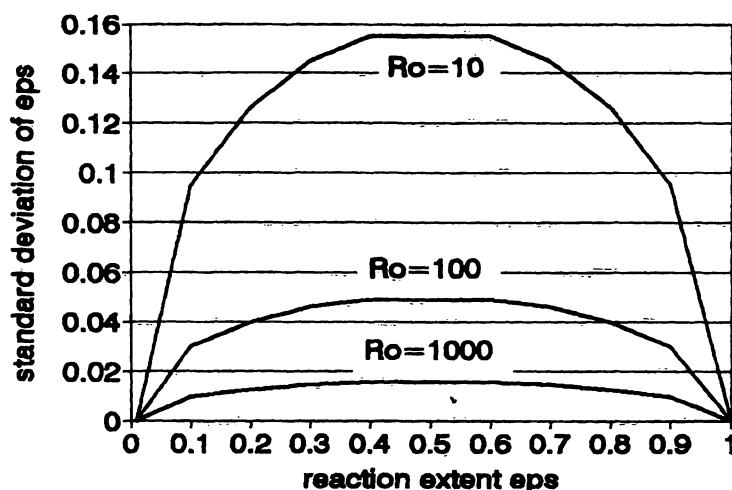


Fig 1: The standard deviation $\sigma(\varepsilon)$ as a function of the reaction extent ε for different values of the initial number R_0 of reactant particles in the control volume.

number of particles R_0 from the control volume influences $t_{0 \rightarrow 1}$. Large values of R_0 make vanish the minimum dwell time necessary to start the reaction. It is convenient to use the notation:

$$\tilde{\tau} = k_f \tau = k'/f \quad (21)$$

where $k' = A1R_0'k_f$. We call $\tilde{\tau}$ the reduced dwell time (the dwell time in k_f units). From eq. (20) we see that $\tilde{\tau}_{\min} = k_f \tau_{\min}$ becomes a function of two parameters only, namely R_0 and r . Numerical evaluations show a negligible dependence of $\tilde{\tau}_{\min}$ on r for reasonably small values of r (i.e. less than unity) and initial number of reactant particles in the control volume $R_0 > 10$.

It is important to point out that classical (deterministic) approaches always associate the start of the reaction with the time $t = 0$. Consequently, they are not able to put into evidence a maximum flow rate which, when exceeded, makes the reaction to stop. However, common practice shows that such a maximum flow rate does exist. The fact that the probabilistic approach is able to predict it is, of course, one of its advantages.

4. Power production

Now let us examine the two arrangements of power generation. The above considerations make it clear that important fluctuations arise only for relatively small systems and/or low fuel concentrations. In practice such situations could arise, for example, in case of the combustion of solid fuels. Then R_0 could denote the initial number of bricks in the control volume. Of course, there is no reverse reaction in this case, and a value $r = 0$ has to be used.

We define two expectation bounds for the fluctuations of the reaction extent, namely ε_{sup} and ε_{inf} :

$$\varepsilon_{\text{sup (inf)}} = \varepsilon_{\text{mean}} \pm \sigma(\varepsilon) \quad (22)$$

Of course, each quantity (say X) depending on ε is characterized by an expected range of values between $X(\varepsilon_{\text{sup}})$ and $X(\varepsilon_{\text{inf}})$.

We should remind that the classical finite-time thermodynamics allows to evaluate the mean value of X only. The probabilistic approach, which allows to define some statistic measures for the fluctuations too (as the expectation bounds above), brings out new information from which one learns more about the system and its operation.

Case I

By using eq. (21) the reaction heat q_r defined in eq. (2) can be put into reduced (dimensionless) form.:

$$\tilde{q}_r \equiv \frac{q_r}{k'Q_p} = \frac{\varepsilon(\tilde{\tau}, r)}{\tilde{\tau}} \quad (23)$$

The mean value $\tilde{q}_{r,\text{mean}}$ is positive only when the reduced dwell time $\tilde{\tau}$ exceeds the value $\tilde{\tau}_{\text{min}} = \tau_{\text{min}} k_f$ where $\tau_{\text{min}} \equiv t_{0 \rightarrow 1}$ is given by eq. (20). Numerical computations show that the reduced reaction heat has a maximum which depends on R_0 and corresponds to a reduced dwell time in the range 0.5 to 1.0; $\tilde{q}_{r,\text{min}}$ vanishes in the limit $\tilde{\tau} \rightarrow \infty$. The upper and lower limits $\tilde{q}_{r,\text{sup}}$ and $\tilde{q}_{r,\text{inf}}$ show qualitatively similar features.

By using the eqs. (3) and (23) we can obtain the reduced form of the heat released per unit amount of fuel spent:

$$\tilde{q}_{r/f} \equiv \frac{q_r}{Q_p f} = \varepsilon(\tilde{\tau}, r). \quad (24)$$

Note that $\tilde{q}_{r/f}$ can be seen as a fuel efficiency. This indicator increases monotonically with the reduced dwell time $\tilde{\tau}$.

Let us focus on the power W supplied by the heat engine. By using eqns. (5) and (21) the reduced power \tilde{W} can be defined as

$$\tilde{W} \equiv \frac{W}{C T_0 k'} = \frac{u \varepsilon(\tilde{\tau}) - \ln[u \varepsilon(\tilde{\tau}) + 1]}{\tilde{\tau}} \quad (25)$$

where the notation $u = Q_p / C T_0$ is used. The time variations of \tilde{W}_{mean} , \tilde{W}_{sup} and \tilde{W}_{inf} are shown in Figure 2 for $u = 1$. All these indicators have a maximum which depends on R_0 . For small values of R_0 the fluctuations of \tilde{W} may be rather big. It is obvious in this case that the information obtained by using the classical approach (the mean value of the reduced power) could give an incomplete image only of what could really happen. At larger dwell time \tilde{W} decreases along with the fluctuations. In the limit $\tilde{\tau} \rightarrow \infty$ the power vanishes. Other computations were performed for the cases $u = 0.1$ and $u = 10$. The above remarks still apply.

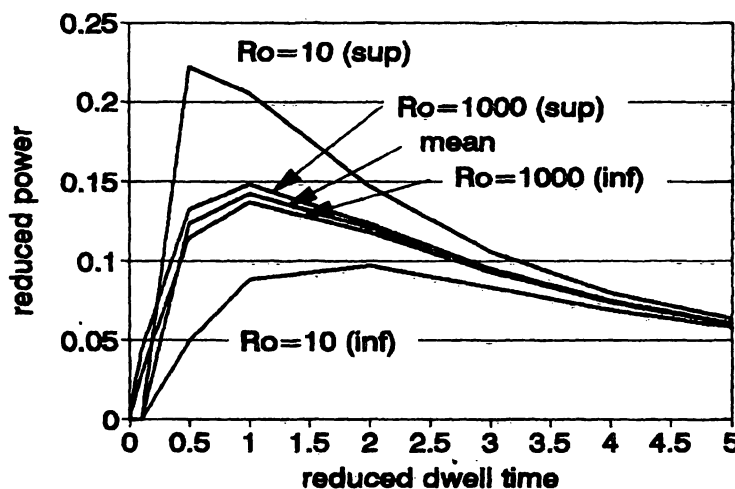


Fig 2: Case I. The mean, the superior bound and the inferior bound of the reduced power (\tilde{W}_{mean} , \tilde{W}_{sup} and \tilde{W}_{inf} , respectively; see eqs. (25), (17) and (22)) as functions of the reduced dwell time $\tilde{\tau}$ (eq. (21)) for different values of the initial number R_0 of reactant particles in the control volume.

Equations (3) and (25) can be used to define the reduced power per unit amount of fuel:

$$\tilde{W}_{/f} \equiv \frac{W}{CT_0 f} u\varepsilon(\tilde{\tau}) - \ln[u\varepsilon(\tilde{\tau}) + 1] \quad (26)$$

Figure 3 shows the time variation of $\tilde{W}_{/f,\text{mean}}$, $\tilde{W}_{/f,\text{sup}}$ and $\tilde{W}_{/f,\text{inf}}$ for $u = 1$. None of these indicators have a local maximum. Each of them reaches its maximum value in the limit $\tilde{\tau} \rightarrow \infty$. This is in agreement with the dependence on $\tilde{\tau}$ of the heat released per unit amount of fuel. The fluctuations of the reduced power per unit amount of fuel are large for smaller values of R_0 . As we see, the actual value of this indicator could be in some cases 20% higher or smaller than the mean value, which is the only information predicted by the classical approach. The above remarks maintain for other values of u .

Case II

Equations (3), (7) and (8) can be used to derive the reduced power \tilde{W} and the reduced power per unit amount of fuel $\tilde{W}_{/f}$:

$$\tilde{W} \equiv \frac{W}{CT_0 k'} = \frac{\eta_{\text{engine}} \left[u\varepsilon(\tilde{\tau}) - \left(\frac{T_H}{T_0} - 1 \right) \right]}{\tilde{\tau}} \quad (27)$$

$$\tilde{W}_{/f} \equiv \frac{W}{CT_0 f} = \eta_{\text{engine}} \left[u\varepsilon(\tilde{\tau}) - \left(\frac{T_H}{T_0} - 1 \right) \right]. \quad (28)$$

Different expressions for the engine efficiency η_{engine} have been derived in the framework of finite-time thermodynamics (see [11]). Here we assume the well known Chambadal-

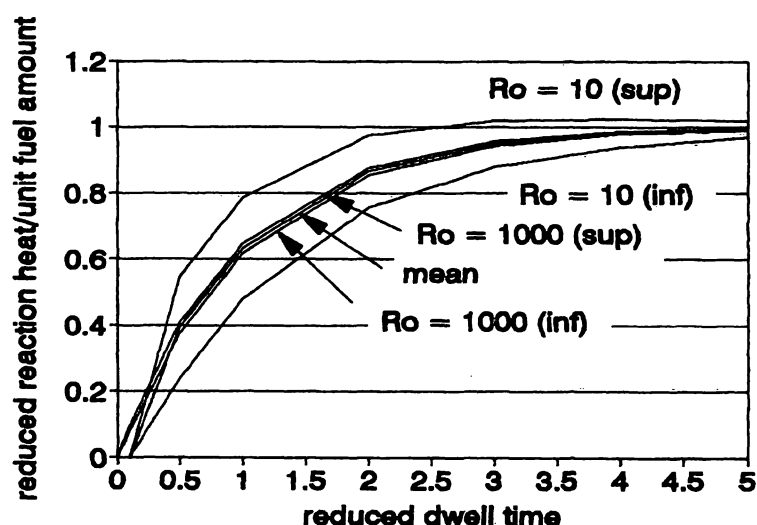


Fig 3: Case I. The mean, the superior bound and the inferior bound of the reduced power per unit amount of fuel ($\tilde{W}_{/f,\text{mean}}$, $\tilde{W}_{/f,\text{sup}}$ and $\tilde{W}_{/f,\text{inf}}$, respectively; see eqs. (26), (17) and (22)) as functions of the reduced dwell time $\tilde{\tau}$ (eq. (21)) for different values of the initial number R_0 of reactant particles in the control volume.

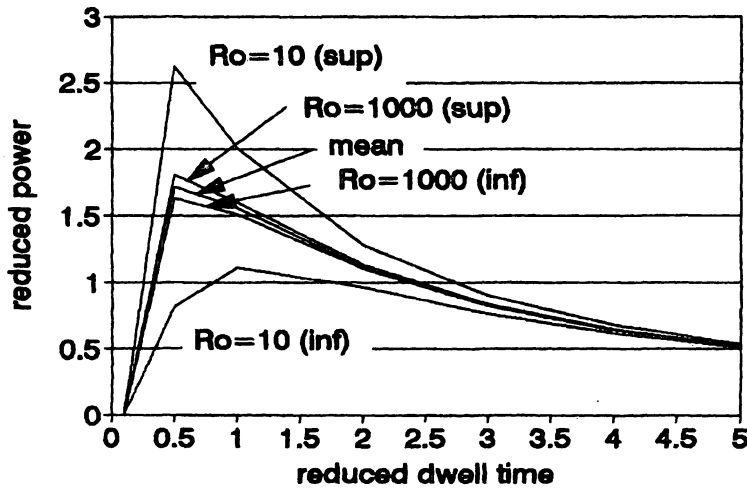


Fig 4: Case II. The mean, the superior bound and the inferior bound of the reduced power (\tilde{W}_{mean} , \tilde{W}_{sup} and \tilde{W}_{inf} , respectively; see eqs. (27), (17) and (22)) as functions of the reduced dwell time $\tilde{\tau}$ (eq. (21)) for different values of the initial number R_0 of reactant particles in the control volume. We assumed $u = 10$ and $T_H/T_0 = 2$.

Novikov-Curzon-Ahlborn (CNCA) efficiency [3, 12]:

$$\eta_{\text{engine}} = 1 - \left(\frac{T_0}{T_H} - 1 \right)^{1/2} \quad (29)$$

Both performance indicators \tilde{W} and \tilde{W}_{fj} can be evaluated for the mean, the superior, and the inferior expectation values by using eqs. (17) and (21). Note that for certain combinations of the parameters u , T_H/T_0 and r the thermal engine cannot supply positive power. I.e. the system is being driven so hard that the engine must act as a heat pump in order to maintain the required temperatures. Figure 4 shows some results obtained for \tilde{W} with $u = 10$ and $T_H/T_0 = 2$. The optimum dwell time when the maximum power occurs depends on R_0 . It is important to note that the fluctuations are larger on the same range of the reduced dwell time where the maximum of the reduced power is obtained. This shows that caution should be taken when the classical approach is used for optimization design. If possible, the probabilistic approach is recommended to be used in this case. In the limit $\tilde{\tau} \rightarrow \infty$ all expectation values vanish. The reduced power per unit amount of fuel increases monotonically with the dwell time. Its time variation is similar to that of \tilde{W}_{fj} shown in Figure 3.

5. Conclusions

The usage of probabilistic concepts allows a fuller description of the performance of a power system. So, each of the usual indicators (power supplied, thermal and exergetic efficiencies, etc.) may first be evaluated in a “mean” approach. Then upper and lower standard expectation values can be estimated. The mean value of any performance indicator is accessible by the usual finite-time thermodynamic methods as treated in this paper, at least in case of linear kinetic processes. The other indicators related to

fluctuations require an appropriate probabilistic model. Of course, when such a probabilistic model exists, it allows the evaluation of the mean values of the performance indicators too.

When the mean value indicator is used, the following conclusions can be drawn. The reaction heat and the reaction heat per unit amount of fuel are strictly decreasing and increasing functions of the dwell time, respectively. There is an optimum dwell time (or flow rate) which maximizes the mean power produced by an engine which has maximum efficiency and which is driven by an exothermic first order chemical reaction. This is true for Case I where the heat of reaction is transferred reversibly to the engine at the reaction temperature $T(f)$ as well as for Case II where the reaction products transfer heat to a reservoir at T_H and then escape at T_H . The mean fuel efficiency W/f is an increasing function of the dwell time.

The probabilistic picture allows one to extract some specific features. There is a minimum dwell time τ_{\min} necessary to start the reaction. When the traversal time τ is smaller than τ_{\min} (i.e. the flow rate f exceeds a certain maximum value f_{\max}) probably the reaction does not start and, consequently, the reaction heat and the power supplied in both cases I and II are zero. The minimum dwell time is larger in case of poor (inferior) fuels. Generally the fluctuations of the estimates are strongly dependent on the initial number R_0 of reactant particles from the control volume. The richer fuels, or the larger systems (where a large control volume could also be defined), are usually associated with smaller fluctuations in the power generation system. The fluctuations are most important at small values of the dwell time (i.e. at large flow rates). This proves the utility of the probabilistic concepts in finite-time thermodynamic theories which are obviously devoted to describing processes characterized by limited duration or, equivalently, by large velocities.

A more realistic treatment of a chemically driven engine requires (i) use of chemical reactions of higher order and (ii) use of temperature dependent rate coefficients. Both of these improvements were already analyzed using deterministic tools [4,5]. Covering (i) and (ii) by a probabilistic method is a difficult task which requires further investigation.

Finally, we mention that there are a number of advanced engineering processes where the use of probabilistic finite-time thermodynamic methods seem to be appropriate. As an illustration and in order to give perspective to our findings we briefly state a few of them without detailed explanation. In the practice of thermal gasification of wood and coal it is known that the reactor has a stable operation for a certain flow range only, while exceeding a maximum flow stops the reaction [13,14]. These experimental facts are qualitatively similar to the results predicted by our theory. So, we expect a specific probabilistic model could be developed in the above case, too. This would allow to derive the best operation conditions for gasification but also some statistic measures for the fluctuations of the products rate. A new technique of solar energy conversion is the free-falling particle receiver, known also as the direct absorption solar receiver [15]. Its design allows the working medium (a large number of small solid falling particles) to be introduced directly into the receiver cavity which is then exposed to the incoming concentrated solar energy. The absorption of radiation by a given particles is a probabilistic process and the receiver cavity plays the role of the reactor from our

model. Indeed, there is a probability for the falling particle to “burn” (i.e. receive and absorb solar radiation during its falling, hence increasing the thermal energy of the working fluid) or not to burn, similar to the probability of a reactant particle to perform or not the first order reaction (eq. (9)) from our model. A third field of interest, not very close to the simple reaction we treated here, is the process of colloidal aggregation with fragmentation which concerns systems with dimensions of nanometres to micrometres (like aerosols, cements, cosmetics, emulsions, foams, paints and plastics). Engineering processes which rely on the application of properties of colloidal systems are adhesion, detergency, grinding or emulsion polymerization. All these processes are usually driven by heat, work and mass transfer through the system boundaries, which should be taken into account during the engineering design. On the other hand, because of their small size, colloidal particles undergo Brownian motion and their aggregation and coagulation should be modeled by statistic methods [16]. So, it is expected an interdependence between the macroscopic fluxes entering or leaving the system and the random behaviour of the microscopic components of the system should exist and it is the purpose of probabilistic finite-time thermodynamics to try to describe it.

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Appendix

A study of eqs. (13) and (14) is performed most conveniently in the generating function representation. We define the generating function $F(s, t)$ by [10, p. 18]

$$F(s, t) = \sum_{P=0}^{R_0} s^P \pi(P, t) \quad (\text{A1})$$

where $|s| \leq 1$ in order to assure convergence. By using (A1) eqs. (13) and (14) take the following form:

$$\frac{\partial F}{\partial t} = k_f R_0 (s - 1) F(s, t) + \frac{\partial F}{\partial s} [k_b + (k_f - k_b)s - k_f s^2]. \quad (\text{A2})$$

This first-order equation with partial derivatives will be solved by realizing that, first, $\pi(P, t)$ must be normalized and, second, The initial condition (15) has to be fulfilled. The first requirement means that

$$F(1, t) = \sum_{P=0}^{R_0} \pi(P, t) = 1 \quad (\text{A3})$$

while the second implies that

$$F(s, 0) = 1. \quad (\text{A4})$$

The characteristic system attached to eq. (A2) is:

$$\frac{dt}{1} = \frac{ds}{-[k_b + (k_f - k_b)s - k_f s^2]} = \frac{dF}{k_f R_0 (s-1)F} \quad (\text{A5})$$

By integrating eq. (A5) one obtains:

$$\ln \frac{e^t}{\left| \frac{s-p}{s-q} \right|^{1/k_f(p-q)}} = C_1 \quad (\text{A6})$$

$$\ln \frac{F \left| \frac{s-p}{s-q} \right|^{[R_0/(p-q)][k_f+k_b]/2k_f}}{|k_f(s-p)(s-q)|^{R_0/2}} = C_2 \quad (\text{A7})$$

where C_1, C_2 are constants while p and q are the roots of the equation $k_f s^2 - (k_f - k_b)s - k_b = 0$.

Equation (A2) has the solution $W(C_1, C_2) = 0$ or, by using eqs. (A6) and (A7)

$$F = \frac{|k_f(s-p)(s-q)|^{R_0/2}}{\left| \frac{s-p}{s-q} \right|^{[R_0/(p-q)][(k_f+k_b)/k_f]}} g \left(\frac{e^t}{\left| \frac{s-p}{s-q} \right|^{1/k_f(p-q)}} \right) \quad (\text{A8})$$

Here W and g are arbitrary functions. The form of g may be determined by using eq. (A4). Then eq. (A8) becomes

$$g \left(\frac{1}{\left| \frac{s-p}{s-q} \right|^{1/k_f(p-q)}} \right) = |k_f(s-p)(s-q)|^{-R_0/2} \left| \frac{s-p}{s-q} \right|^{[R_0/(p-q)][(k_f+k_b)/2k_f]} \equiv y. \quad (\text{A9})$$

From eq. (A9) one obtains

$$x = g^{-1}(y) = \frac{1}{\left| \frac{s-p}{s-q} \right|^{1/k_f(p-q)}} \quad (\text{A10})$$

where g^{-1} is the inverse of the function g . This may be rewritten as

$$s = \frac{px^{k_f(p-q)} - q}{x^{k_f(p-q)} - 1}. \quad (\text{A11})$$

Consequently

$$y = \left| \frac{k_f(p-q)^2}{[x^{k_f(p-q)} - 1]^2} x^{k_f(p-q)} \right|^{-R_0/2} |x|^{-R_0(k_f+k_b)/2}. \quad (\text{A12})$$

But eq. (A10) shows that

$$y = g(x) \quad g^{-1}(y) = x. \quad (\text{A13})$$

By using eqs. (A8), (A10), (A12) and (A13) one obtains:

$$F(s, t) = \frac{1}{(p - q)^{R_0}} \left| |s - q| e^{k_f(p - q)t} - |s - p| \right|^{R_0} e^{-R_0[k_f(p - q) + (k_f + k_b)]t/2} \quad (\text{A14})$$

Now we use the normalizing condition (A3) to get

$$\frac{e^{-R_0[k_f(p - q) + (k_f + k_b)]t/2}}{(p - q)^{R_0}} = \frac{1}{\left| |1 - q| e^{k_f(p - q)t} - |1 - p| \right|^{R_0}}. \quad (\text{A15})$$

Combining eqs. (A14) and (A15) one obtains

$$F(s, t) = \left| \frac{|s - q| e^{k_f(p - q)t} - |s - p|}{|1 - q| e^{k_f(p - q)t} - |1 - p|} \right|^{R_0} \quad (\text{A16})$$

The final form of $F(s, t)$ can be derived by using the definitions of p and q :

$$F(s, t) = \left[\frac{k_f}{k_f + k_b} \left| s + \frac{k_b}{k_f} \right| - |s - 1| e^{-(k_f + k_b)t} \right]^{R_0}. \quad (\text{A17})$$

The generating function can be used to determine the stochastic function $\pi(P, t)$ [10, p 442] by

$$\pi(P, t) = F^{(P)}(0, t)/P! \quad P = 0, 1, \dots, R_0. \quad (\text{A18})$$

By performing these computations we obtain eq. (16). The generating function can be used to determine the mean value P_{mean} and the variance $D^2(P(t))$ [10, p440] through

$$P_{\text{mean}} = \left. \frac{\partial F}{\partial s} \right|_{s=1} \quad (\text{A19})$$

$$D^2(P(t)) = \left. \left(\frac{\partial^2 F}{\partial s^2} + \frac{\partial F}{\partial s} - \left(\frac{\partial F}{\partial s} \right)^2 \right) \right|_{s=1}. \quad (\text{A20})$$

By using eqs. (A16), (A19) and (A20) we obtain

$$P_{\text{mean}} = R_0 \frac{k_f}{k_f + k_b} [1 - e^{-(k_f + k_b)t}] \quad (\text{A21})$$

$$D^2(P(t)) = P_{\text{mean}} \left(1 - \frac{P_{\text{mean}}}{R_0} \right). \quad (\text{A22})$$

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