Eur. Phys. J. B **29**, 117–121 (2002)
DOI: 10.1140/epjb/e2002-00268-8

THE EUROPEAN PHYSICAL JOURNAL B

Efficiency of a stirred chemical reaction in a closed vessel

C. López[1,a], D. Vergni[1,2], and A. Vulpiani[1,2]

[1] Dipartimento di Fisica, Università di Roma 'La Sapienza', P.le A. Moro 2, 00185, Roma, Italy
[2] INFM UdR and SMC Roma 'La Sapienza', P.le A. Moro 2, 00185, Roma, Italy

Received 20 June 2002 / Received in final form 9 July 2002
Published online 17 September 2002 –

Abstract. We perform a numerical study of the burning efficiency in a closed vessel. Starting with a little spot of product, we compute the time needed to complete the reaction in the container. Inside the vessel there is a cellular flow that transports the reactants. Our main result is that if the size of the container is not very large compared with the typical length of the velocity field, one has a plateau of the burning time as a function of the strength of the velocity field, U. This means that, once the plateau is reached, a further increase of U does not reduce the time needed to complete the reaction. This plateau arises when we consider both a stationary and a time-dependent cellular flow, and we give analytical and numerical arguments that try to explain why it appears. Also a comparison of the results for the finite system with the infinite case shows the dramatic effect of the finite size.

PACS. 05.45.-a Nonlinear dynamics and nonlinear dynamical systems – 47.70.Fw Chemically reactive flows

Numerous physical, biological and chemical systems show the propagation of a stable phase into an unstable one [1,2]. When this phenomenon takes place in a fluid, one generally speaks of front propagation in advection-reaction-diffusion (ARD) systems. Under this generic name one indicates many different processes, *e.g.*, the propagation of plankton populations in ocean currents [3], the transport of reacting pollutants in the atmosphere (*e.g.* ozone) [4], the effect of stirring on complex chemical reactions [5], or combustion [6].

In the last years much effort has been done to study the influence of an advection field on the front dynamics. In particular, it is well established that the front speed in a laminar or turbulent fluid is enhanced with respect to the propagation in a medium at rest [7,8]. In the context of (premixed) combustion processes the flame front area is proportional to the front speed and, therefore, an increasing of the front area due to the fluid stirring gives rise to an enhancement of the burning efficiency, that is, the *system burns faster*.

It is important to note that most of the theoretical studies and, in particular, the above results about the enhancement of the burning efficiency, have been shown for an infinite-size system (in the propagation direction). Also, asymptotic quantities like the front speed are only properly defined for infinite (or with periodic boundary conditions) systems.

[a] e-mail: cristobal.lopez@phys.uniroma1.it

On the other hand, from a practical point of view one usually has to treat cases where the size of the domain is not much larger than the typical length scale of the velocity field [9]. The spreading of organisms in a lake or in a small closed sea basin, and the combustion of fuel in a machine motor are two clear examples where this may happen and, therefore, non-asymptotic properties can be very important [10,11].

In this work we treat the case of an ARD process confined in a closed region. Beginning with a small quantity of material in the stable phase (also called burnt material), we numerically compute the time needed for a given percentage of the total region to be also burnt (called in the following, the burning time). The velocity field is of cellular flow type, *i.e.*, it is formed by circulating cells of fluid. Both, a stationary and a chaotic time-dependent cellular flow will be considered. Our main result, obtained either for the time-independent and for the time-dependent case, is that increasing the typical velocity of the field one has a saturation of the burning rate. This saturation happens when the advection time scale is much shorter than the reaction time scale. Also, we compare our results with the infinite-size case, studying the crossover from finite size systems to the asymptotic regime. We observe that the relevance of the system size is more important than expected *a priori*.

Let us consider the simplest non trivial case described by a scalar field $\theta(\mathbf{x}, t)$ which represents the concentration of reaction products, such that θ is equal one in the

space-time coordinates where the reaction is over (the stable phase), and θ is zero where there is fresh material (the unstable phase). The dynamical evolution of this field is given by

$$\partial_t \theta + \mathbf{v} \cdot \nabla \theta = D \nabla^2 \theta + \frac{f(\theta)}{\tau}, \tag{1}$$

where $\mathbf{v}(\mathbf{x}, t)$ is a two-dimensional incompressible velocity field, D is the diffusion coefficient, and $f(\theta)$ is the reaction term, where τ is the time scale for the reaction activity. For the reaction term we use the Fisher-Kolmogorov-Petrovskii-Piskunov (FKPP) nonlinearity [12], $f(\theta) = \theta(1-\theta)$. Concerning the velocity field, $\mathbf{v}$, we first adopt a simple stationary incompressible two-dimensional flow defined by the stream-function

$$\psi(x, y) = \frac{UL}{\pi} \sin\left(\frac{\pi x}{L}\right) \sin\left(\frac{\pi y}{L}\right), \tag{2}$$

being the parameter U the maximum vertical velocity of the flow, and L the size of one cell. For a study of the transport properties in the field (2) see reference [13]; the asymptotic behaviour of front propagation is discussed in reference [15]. The equations of motion for a fluid element are given by

$$\begin{cases} \dot{x} = \quad \partial_y \psi \\ \dot{y} = -\partial_x \psi. \end{cases} \tag{3}$$

In this work the reaction processes described by (1) take place in a closed recipient. This confinement is implemented by assuming rigid boundary conditions on the box $0 \leq y \leq L$ and $0 \leq x \leq nL$, where n is the number of circulating cells of the flow. One approaches to the asymptotic case increasing the value of n.

The settling of the problem is completed when we indicate the initial conditions, in our case a small initial spot of burnt material which starts the reaction. Thus, we use in all our numerical experiments a small circle of radius r filled with stable material, that is placed at the initial time in the box filled with unstable material. The initial coordinates of the center of this circle are $(x = r, y = L/2)$ (the circle is on the border of the box; this mimics the injection of reacting material from the outside). As anticipated, the principal observable under investigation is the time needed for a given percentage of the total area to be burnt. We define $S(t) = \frac{1}{\Delta S} \int_{\Delta S} \mathrm{d}x\mathrm{d}y\theta(x, y, t)$ as the percentage of area burnt at time t, where $\Delta S = L^2 n$ is the total area of the container. In our case, by choosing an appropriate r the initial burnt material is $S(0) = 0.005/n$, which is the 0.5% of one cell. The burning time t_α is defined as the time needed for the percentage α of the total area of the recipient to be burnt, *i.e.*, $S(t_\alpha) = \alpha$.

Numerically, to integrate (1) we use the Feynman-Kac (FK) or stochastic Lagrangian approach. This algorithm is based on the relation between ARD systems and the Langevin equation describing the evolution of test particles under the combined influence of the velocity field and the Brownian motion [14]. The field evolution is computed using the Lagrangian propagator plus a Monte-Carlo integration for the diffusive term. Then, the reaction propagator accounts for the reacting term (for details see [15,16]). We also impose a rigid wall condition in the boundaries. In the following we assume $L = \pi$ and $D = 0.04$.

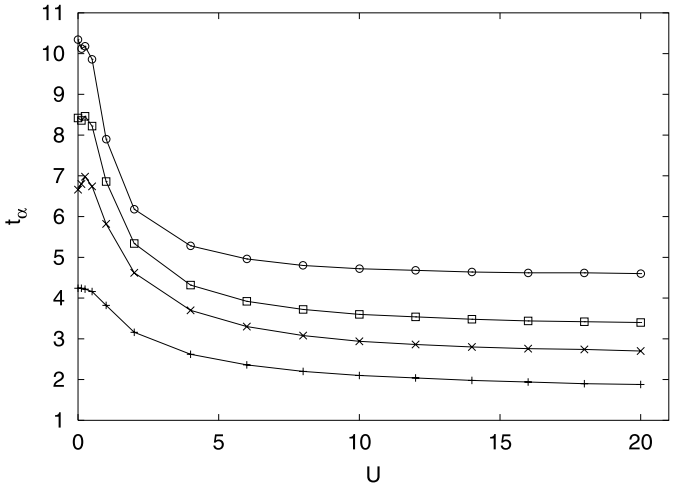

Fig. 1. t_α against the flow strength U with $\tau = 0.4$, $n = 1$ and for various α: $\alpha = 0.2$ (+), $\alpha = 0.5$ (×), $\alpha = 0.7$ (□), $\alpha = 0.9$ (○).

We first show in Figure 1 the influence of the stirring intensity on the burning efficiency, when different percentages, α, of the final burnt area are considered.

Increasing the maximum velocity of the flow, U, t_α decreases monotonically until a plateau is reached. Then, a further increasing of the flow velocity does not decrease the burning time t_α. We remark that this effect also appears for different finite values of the system size (different values of n), and different chemical rates τ. At first glance, the appearance of the plateau seems to be surprising: *in a closed container the burning efficiency is not always improved by increasing the stirring intensity.*

The existence of the plateau can be understood noting that it is reached only when the reaction time, τ, is large compared with the advection time, $\tau_a = L/U$. In this case, in the first stages of the process (in which only a small fraction of the volume is active), because of advection and diffusion the active material has a rapid spreading and invades the whole container with value of θ small but different from zero. Then, because of the reaction term, one has an exponential increasing of the value of θ all over the cell, until it is completely burned. In this two step process, spreading and reaction, the increasing of the stirring intensity do not correspond to an increasing of the burning efficiency.

A direct comparison between the finite and the infinite system is interesting. In Figure 2 we show the burning time scaled with the system size, *i.e.*, t_α/n, against the typical flow velocity, U, for some values of n. We also plot the data obtained for an infinite system, which have been

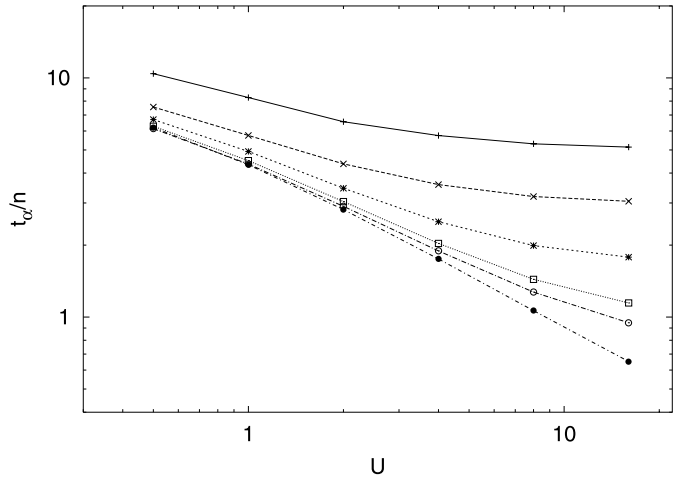

Fig. 2. The burning time per unit-cell, t_α/n, at various U for $\tau = 0.4$ and $\alpha = 0.9$. The plots are for different system's sizes: $n = 1$ (+), $n = 2$ (×), $n = 4$ (∗), $n = 8$ (□) and $n = 12$ (○). It is also shown (•) the burning time calculated using the front speed: $t = nL/v_f$.

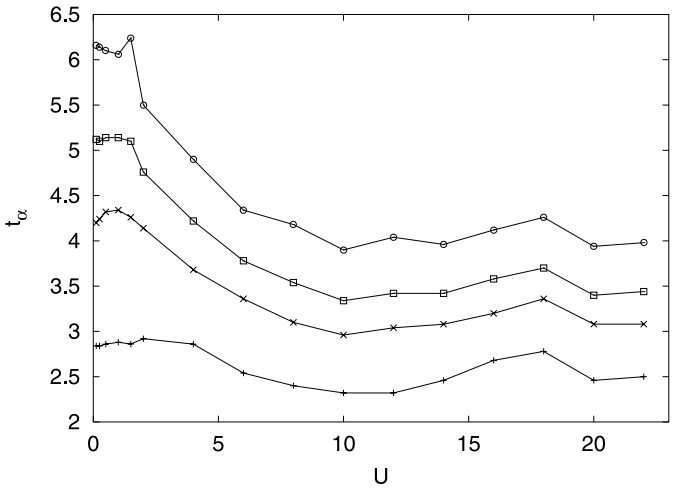

Fig. 3. t_α against the flow strength U for various α in the unsteady case ($B = 1.1$ and $\omega = 2.09$): $\alpha = 0.2$ (+), $\alpha = 0.5$ (×), $\alpha = 0.7$ (□), $\alpha = 0.9$ (○). The flow is confined in two cells and $\tau = 0.4$.

calculated from the front speed v_f of the infinite system data according to

$$t_\alpha \simeq \frac{nL}{v_f}, \tag{4}$$

which is expected to hold for α close to 1 and large n.

Figure 2 shows that the asymptotic reacting time (given by v_f) is reached only in the large size limit, *i.e.*, n large, while the dynamics of small systems is dominated by the non asymptotic properties of the evolution.

Since the considered bidimensional velocity field (2) is stationary the Lagrangian trajectories are not chaotic. Nevertheless also in the case of Lagrangian chaotic trajectories, obtained with a time-dependent flow, the burning time shows the same qualitative behaviours shown in Figures 1 and 2. Let us consider a time-dependent flow whose stream function is

$$\psi(x, y, t) = U \sin(x + B(x)\cos(\omega t))\sin(y)\,. \tag{5}$$

This is sufficient to induce Lagrangian chaos [17] in the evolution of passive tracers advected by the velocity field (3) generated by (5). Because we are dealing with closed systems $B(x)$ is constructed in such a way that it is zero near the boundary of the system and almost constant, B_0, otherwise: $B(x) = B_0(1-\exp(-1/x)-\exp(-1/(nL-x)))$.

In Figure 3 we show the curve t_α against U for different values of α. At difference from the previous case, when unsteady flow is concerned there is not a simple plateau in t_α, but an oscillatory behaviour due to the interplay between the oscillation period of the separatrices and the circulation time inside the cell. It happens that circulation and oscillation "synchronize" producing a very efficient and coherent way of transferring passive particles from one cell to the other. A similar, but much more impressive, feature occurs for the effective diffusion coefficient in the horizontal direction [18]. Comparing Figures 2 and 3 one has that for low values of U the mixing induced by the time dependence makes that the system burns quite faster. For higher U, the mixing properties of the flow are not sufficient to improve furthermore the burning efficiency. Also in this case the physical reason for the presence of the plateau at large U is due to a time separation between the initial spreading and reaction mechanisms. The only difference is that the spreading time is smaller and the plateau appears sooner.

Let us study the dependence of the *saturation time* $t^s_\alpha(\tau)$, which is the value of the burning time in the plateau, as a function of τ. In the unsteady case, we choose as saturation time the minimum value of t_α at varying U.

In Figure 4 we show the result for the unsteady case, which can be interpreted following the same arguments used to explain the existence of the plateau. As we have previously noted, the system dynamics in the case of large U can be divided in two parts: the initial spreading regime and the reacting dominated regime. This implies, together with a dimensional argument, $t^s_\alpha(\tau) = \tilde{t} + b_\alpha\tau$, where $\tilde{t}$ is the spreading time. Thus, there is a linear dependence of t^s_α with τ as shown in Figure 4, which has been obtained for the time-dependent flow, but similar results hold also for the steady case.

The value of the slope of the saturation time against τ, b_α, can be analytically studied. In the regime of very high U such that the plateau is reached, after the time $\tilde{t}$ the initial condition is spread out through the whole container and one can approximate $\theta(x, y, t) \sim \tilde{\theta}(t)$, being $\tilde{\theta}(t)$ a rough average of the θ field in the container, which evolves following only the reaction part of (1). This is because, as we have argued before, after $\tilde{t}$ the important physical mechanism of burning comes from the chemical activity and not from the mixing due to the advection and

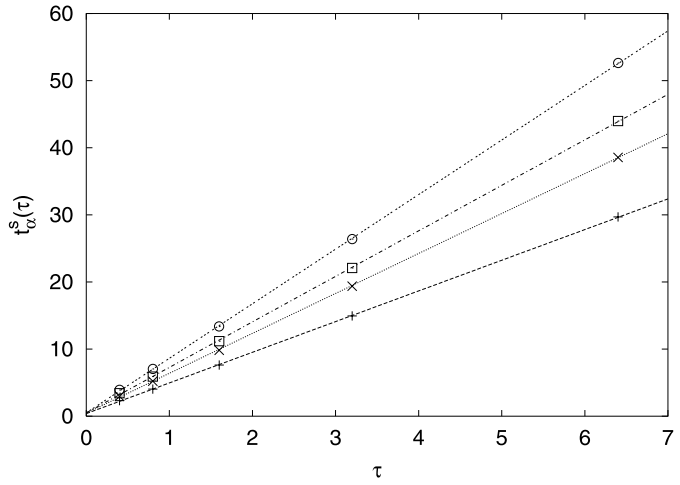

Fig. 4. Plot of $t^s_\alpha(\tau)$ *vs.* τ at various percentages of filling α in the time-dependent case ($B = 1.1$ and $\omega = 2.09$): $\alpha = 0.2$ (+), $\alpha = 0.5$ (×), $\alpha = 0.7$ (□), $\alpha = 0.9$ (○). For each curve we have superimposed the linear fit $t^s_\alpha(\tau) = \tilde{t} + b_\alpha \tau$, where $\tilde{t}$ and b_α are fitting parameters. Here $n = 2$.

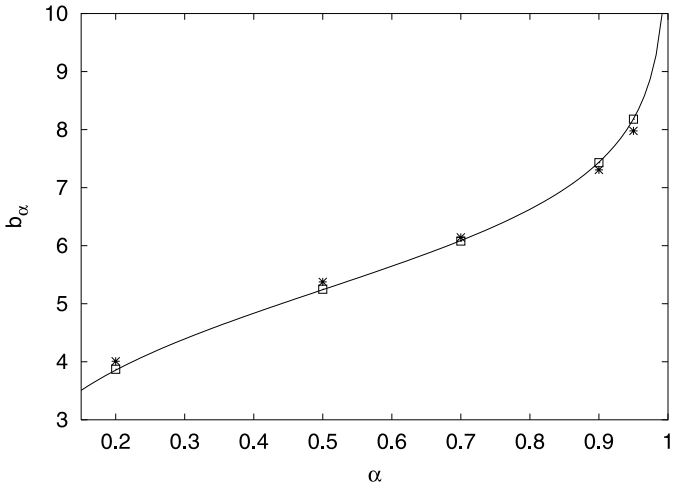

Fig. 5. The slope, b_α, of the saturation time t^s_α against τ, that is, the slope of the curves in Figure 4 (with an additional value for $\alpha = 0.95$), *vs* the percentage α. With (□) the numerical values for time-dependent flow, with (∗) the numerical value (rescaled) for steady flow, and with the solid line the prediction given by (8).

diffusion. Then $S(t) = \tilde{\theta}(t)$ for $t > \tilde{t}$, and so:

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{1}{\tau} S(1 - S). \tag{6}$$

This can be integrated from $\tilde{t}$ to t, taking into account that we can approximate $S(\tilde{t}) \sim S(0)$, *i.e.*, in the spreading regime we can suppose that the reaction does not act. Therefore, one has

$$\log\left(\frac{S(t)}{1 - S(t)}\right) - \log\left(\frac{S(0)}{1 - S(0)}\right) = \frac{t - \tilde{t}}{\tau}\,. \tag{7}$$

Finally, as $S(t^s_\alpha) = \alpha$ we get

$$t^s_\alpha = \tilde{t} + \tau \log\left(\frac{\alpha(1 - S(0))}{(1 - \alpha)S(0)}\right) \equiv \tilde{t} + b_\alpha \tau\ , \tag{8}$$

which gives the dependence of b_α on the percentage of burnt material, α.

For the time-independent cellular flow the reasonings follow closely the former ones. Let us just note that, in this case, because the mixing effect across the streamlines is only due to the diffusion term, the above approximation is particularly rough. Nevertheless, equation (8) is in excellent agreement with the numerical results, see Figure 5, confirming once again the picture presented in this paper.

Summarizing, we have performed a numerical study of an advection-reaction-diffusion system confined in a closed vessel, using stationary and time-dependent cellular flows. Beginning with a small quantity of the active phase, we have calculated the time needed for a percentage of the total area to be burnt. Thus, our numerical experiments may represent the spreading of an organism in a lake or the combustion of a material in a vessel. The main lesson to learn from our studies is that the influence of the system size is very important [19]. In particular, we have shown that for large stirring intensity compared with the reaction time, the burning time saturates, giving rise to the unexpected result that increasing furthermore the flow velocity there is not an improvement of the burning efficiency. Moreover we have shown that the burning time in the plateau is proportional to the reaction time-scale. Let us note that when there is no clear scale separation between the characteristic time of spreading and reaction, the dynamics could be very complicated, and one cannot found a general behaviour. To conclude, we have to mention that a similar scenario, *i.e.*, the appearance of the plateau in the burning time, has been obtained for other types of chemical reactions $f(\theta)$, like the Arrhenius $f(\theta) = (1 - \theta)\exp(-\theta_0/\theta)$ (θ_0 constant) or the Zeldovich function $f(\theta) = \theta^2(1 - \theta)$.

This work has been partially supported by INFM *Parallel Computing Initiative* and *MURST (Cofinanziamento Fisica Statistica di Sistemi Complessi Classici e Quantistici)*. C.L. acknowledges support from MECD of Spain, D.V and A.V. acknowledge support from the INFM Center for Statistical Mechanics and Complexity (SMC).

References

1. J. Xin, SIAM Review **42**, 161 (2000)
2. J.D. Murray, *Mathematical Biology*, 2nd edn. (Springer-Verlag 1993)
3. *Spatial patterns in plankton communities*, edited by J.H. Steele, (Plenum Press, New York, 1978)
4. I.R. Epstein, Nature **374**, 231 (1995)
5. I. Nagypal, I.R. Epstein, J. Phys. Chem. **90**, 6285 (1986); M. Menzinger *et al.*, J. Phys. Chem. **91**, 4391 (1987)

6. N. Peters, *Turbulent combustion* (Cambridge University Press, 2000)
7. P. Constantin, A. Kiselev, A. Oberman, L. Ryzhik, Arch. Rational Mechanics **154**, 53 (2000)
8. A. Kiselev, L. Ryzhik, Ann. I.H. Poincaré **18**, 309 (2001)
9. G. Boffetta, A. Celani, M. Cencini, G. Lacorata, A. Vulpiani, Chaos **10**, 50 (2000)
10. P. Rys, Chimia **46**, 469 (1992)
11. A. Gorczakowski, A. Zawadzki, J. Jarosinski, B. Veyssiere, Combust. Flame **120**, 359 (2000)
12. A.N. Kolmogorov, I.G. Petrovskii, N.S. Piskunov, Moscow Univ. Bull. Math. **1**, 1 (1937) R.A. Fischer, Ann. Eugenics **7**, 355 (1937)
13. T.H. Solomon, J.P. Gollub, Phys. Rev. A **38**, 6280 (1988)
14. M. Freidlin, *Markov Processes and Differential Equations* (Birkhauser, Boston, 1996)
15. M. Abel, A. Celani, D. Vergni, A. Vulpiani, Phys. Rev. E **64**, 046307 (2001)
16. U. Frisch, A. Mazzino, A. Noullez, M. Vergassola, Phys. Fluids **11**, 2178 (1999)
17. H. Aref, J. Fluid Mech. **143**, 1 (1984); A. Crisanti, M. Falcioni, G. Paladin, A. Vulpiani, Riv. Nuovo Cimento **14**, 1 (1991)
18. P. Castiglione, A. Crisanti, A. Mazzino, M. Vergassola, A. Vulpiani, J. Phys. A **31**, 7197 (1998)
19. A different phenomenon where the influence of the system size is also very important is reported in M.V. Tretyakov, S. Fedotov, Physica D **159**, 190 (2001)