Abstract

A 3d microscale numerical tool for the simulation of smoldering in fixed beds of solid fuels is presented. The description is based on the local equations and fully preserves the coupling of the transport and reaction mechanisms. A set of simulations demonstrates the ability of the model to handle a variety of situations, with non trivial chemical scheme, and to provide detailed local information. A phenomenological chart is established, depending on a few dimensionless numbers, which exhibit very different regimes and provides guidelines for the practical operation of a reactor and for a macroscopic homogenized description.

Introduction

We have been addressing the numerical simulation of smoldering in fixed beds of solid fuels for several years, with a twofold objective. We wanted first to build up a fairly general simulation tool on the microscale, and to apply it to investigate various situations. Second, we intended to use the acquired knowledge to answer fundamental questions relative to the relationship between the local mechanisms and the global behaviors, and to the form and actual implementation of a macroscopic description. This paper surveys the main results and conclusions which have resulted from this project.

Any mathematical model of filtration combustion should at least contain governing equations for the gas flow and for the transport of the oxidizer that it conveys, a heat transport equation and a more or less sophisticated model for the chemical reaction kinetics. Obviously, these equations are strongly coupled and non linear. A detailed statement of the problem at the microscale is provided by [1].

When a macroscopic point of view is adopted, the medium is regarded as a continuum [2], the equations involve effective parameters such as mean volumetric reaction rates, and they relate macroscopic fields that represent volume averaged local quantities. However, even assuming that such an upscaled description is applicable, the effective coefficients depend both on the medium microstructure and on the flow and reaction regimes and their determination of is by no means trivial. It generally requires the solution of the full set of microscale equations in a representative sample [3]. In addition, the validity of homogenized equations is restricted to situations where the physical quantities vary smoothly at the macroscale. This condition is violated in many practical situations where a relatively thin reaction front exists, across which temperature may jump by hundreds of degrees. Finally, a formulation in terms of locally averaged quantities generally makes use of a hypothesis of local thermodynamic equilibrium. Whether this condition is met or not can only be determined by the examination of the process on the microscopic scale [4].

Let us illustrate this by a few examples. Suppose that the rate $\xi$ of an oxidative reaction on the solid surface is proportional to the concentration $c_o$ and dependent on temperature $T$. The simplest macroscopic formulation makes use of the locally volume averaged quantities $\bar{c}_o$ and $\bar{T}$. However, in hot regions, the reaction is often diffusion limited, by the oxidizer supply from the bulk of the gas phase. Hence, $c_o$ at the reaction site differs from $\bar{c}_o$. An idea
is to define an additional field $c_{0.5}$, representing the concentration at the solid surface, to be used in the estimation of $\xi$, and related to $c_o$ by an effective transfer coefficient. Alternatively, $\xi$ can be related directly to $c_o$ by an effective volumetric reaction coefficient. These effective coefficients depend on the microstructure and on the flow conditions. Similarly, strong fluctuations of the temperature may take place on the local scale, which makes $T$ unrepresentative of the reaction conditions. Two-field descriptions are often used in macroscopic models, with $T_s$ and $T_g$ representing mean solid and gas temperatures, and related by an effective transfer coefficient. However, due to the localized heat production, the temperature at the reaction site may differ significantly from both of these mean values, and this determines not only the reaction rate but also possibly the nature of the reaction products.

None of these questions can be fully answered from macroscopic approaches, since they already incorporate assumptions about the answers. It is therefore important, and this is the motivation of our effort, to conduct investigations at the local scale, in order to at least determine under which conditions the usual models are applicable, to evaluate the associated effective coefficients, and possibly to go one step beyond, and provide phenomenological indications and modeling guidelines for less amenable situations.

This paper is organized as follows. The focus is set on the results and on their interpretation rather than on the modeling details, which can all be found elsewhere. The physical and mathematical model is described first. In spite of necessary simplifications, we preserve the main feature that we want to investigate, that is the coupling at the microscale of the transport and reaction processes. The numerical implementation is described only very briefly. Then, the conclusions of extensive simulations with the simplest one-reaction chemical model are presented, providing a phenomenological overview of the smoldering regimes. Next, the chemical model is extended by including pyrolytic reactions. Finally, results are presented for a model with a more complex oxidative reaction scheme, and new behaviors are identified, which may call for different macroscopic modeling approaches.

**The physical and numerical models**

Let us start with a few preliminary remarks. This work was supported by a programme of the French Fonds National de la Science. In this framework, two other teams worked in parallel with us, along experimental [5] and macroscopic modeling [6] approaches, although these aspects are not discussed here. All of us used as a starting point and reference situation the set-up, material and operating parameters corresponding to a lab experiment, of co-flow smoldering in a packed bed of grains. The physicochemical parameters are set in the simulations according to their actual values, or to their best available estimate. The grains are oil shale. This material was chosen for its intrinsic interest as a fossil energy resource, and because of a feature which makes it a convenient model material: due to the important mineral matrix, the bed geometry is not significantly modified during the process. This greatly simplifies the simulations, and allows to focus the effort on the description of the transport and reaction mechanisms.

The model is described only very briefly here. Its main features for the version with the simplest chemical model have been outlined in [7] and described in full details in [8,9]. Later improvements are described in [10]. The mathematical model involves governing equations for the gas flow, for the gaseous species and heat transports, a balance equation for the fuel in the grains and a kinetic model for the chemical reactions, which take place in the gas or at the grain surfaces. The problem is very complex, and approximations of various natures are used, which are detailed in the aforementioned references.

Consider first the thermomechanical model. The gas flow is described by Stokes equation, with a no-slip condition on the solid. Inertial effects and property dependence on temperature are ignored. The transport of the species $O_2$, CO and $CO_2$ conveyed by the gas is described by
a convection-diffusion equation. Source and sink terms exist, in the gas phase or at the solid surface, due to the chemical reactions. Heat transport obeys a conduction equation in the solid, and a convection-diffusion in the gas, coupled by temperature and flux matches at the interfaces. Again, source and sink terms occur according to the chemical processes. The balance equations for the immobile solid species, kerogen, char and carbonates, reduce to the account of their production/destruction by the chemical reactions.

Several successive versions of the chemical model have been implemented. Only the initial and simplest one [8,9] is described here. Later improvements are addressed in the corresponding sections below. Pyrolytic reactions are not taken into account. We consider only the oxidation of the char left within the grains by the kerogen cracking by using a "black-box" approach ("one-film model" of [11]). It is likely that CO is produced in a first step, which is later converted into CO2 in the gas phase. We assume that the second step is fast, and summarize the whole scheme by a single exothermal reaction on the grain surface

\[ C + O_2 \rightarrow CO_2 + q \]  

(1)

The reaction kinetic is supposed to be of first order with respect to O2, with a rate coefficient given by Arrhenius law (as long as the fuel is not exhausted). Furthermore, the activation energy \(E\) is supposed to be large enough, so that a sharp transition exists between a low-temperature kinetically controlled regime, with very small reaction rate, and a high-temperature diffusion-limited one. Thus, the kinetic law finally reduces to the bimodal model

\[
\begin{cases}
\text{negligible reaction,} & \text{if } T < T_r \\
\text{diffusion limited reaction,} & \text{if } T \geq T_r
\end{cases}
\]  

(2)

Hence, the processes are described in details by local equations, on the microscopic pore/grain scale. The numerical code implements this model in a full 3d, transient formulation. Again, all details can be found in the afore-mentioned references. Let us just mention that a finite volume method is applied for the flow solution and for the all transfers within the solid, while a random walk approach is applied for the description of all the transports in the gas, with the mobile species or heat represented by random walkers.

Figure 1. Temperature fields for smoldering simulations in a 3d grain packing, with PeO=10 [9]. Air flows in the ascending direction. Distances are measured in grain diameter \(\Phi\). The oil shale is mixed (left) or not (right) with 50% of inert sand. The front position is \(X_f = 26\) or \(17\ \Phi\), respectively.
The chemical reactions are handled by probabilistic production/removal of particles, according to the appropriate kinetic and stoichiometric laws. The simulations are run in a digital image of the porous medium, made of an array of elementary cubic volume elements. Although the code is fully 3d, most of the results presented in the following are in 2d situations. This is because it allowed for a faster sweep of the parameters, especially for the more time consuming simulations with the most elaborate chemical model, and also for an easier graphical display of the results. However, Fig. 1 provides examples of 3d simulations.

The simulations are started with the whole system at room temperature. The shale grains can be mixed with inert sand, as done in the physical experiments. After ignition, a transient period takes place, which is disregarded, followed by the establishment of a stationary regime, where a reaction front progresses with constant velocity.

**Main smoldering regimes and governing parameters**

Extensive simulations have been conducted using this chemical model, and a phenomenological classification into various regimes could be established, depending on three dimensionless numbers. Most interestingly, these numbers can be evaluated a priori, based on the operation conditions and on global characteristics of the materials.

Let us start by a few global remarks. In the stationary regime, a relatively narrow reaction zone, with mean position \( X_F \), propagates with a velocity \( U_F \). This is where the fresh air meets grains which still contain fuel. Upstream of this front, the fuel in the grains is exhausted. In the conditions of the experiment, and in the absence of transverse heat losses, the temperature upstream of \( X_F \) settles at a plateau value \( T_p \). On the downstream side of \( X_F \), it decreases exponentially (as discussed below, the situation can be reverted for different system compositions). An illustration of this typical profile can be seen in Fig. 5.

The first crucial dimensionless parameter is the Péclet number \( Pe_O \) which can be used as a measure of the air supply rate:

\[
Pe = \frac{v^* L}{D_O}
\]

where \( v^* \) is the mean interstitial gas velocity, \( L \) is a characteristic microscale (the grain diameter in 3d random packings, the length of the periodic pattern in the 2d networks of cylinders, or the channel aperture in layered media) and \( D_O \) the oxygen diffusion coefficient. It compares the characteristic times for oxygen diffusion and convection in the conveying gas. When it increases (because of a larger gas flow rate), the oxidizer is carried further away through the medium before it can reach by diffusion the reactive solid surface, as illustrated in Fig. 2. This spreads the reaction zone and the decay lengths for the mean temperature and concentration profiles. Note however that this is a local effect. The only macroscopic consequence is about the reaction front velocity, which is proportional to the oxidizer supply, i.e. to \( Pe_O \). In most cases, the temperature level remains high enough over a sufficient distance for all the fuel and oxygen to be eventually consumed. Hence, the global thermal balance is identical and the plateau temperature \( T_p \) is unaffected. Of course, this would break down for excessive flow rates (\( Pe_O >> 1 \)) which could allow part of the oxygen to escape the hot zone before it could migrate to the solid by diffusion, thereby decreasing the net heat production rate and slowing down the front propagation.

The second important dimensionless parameter \( \Delta \) compares the convective heat flow rate in the gas to the elevation rate of the solid heat contents. It may seem impossible to foretell the value of \( \Delta \) before actually conducting an experiment or its simulation, and this is partly true. However, under the assumption that the reaction is nearly total, which is well verified in practice, the reaction front velocity can be predicted from stoichiometric considerations, and \( \Delta \) can be directly related to physical and compositional parameters which are known a priori,
Figure 2. Temperature and concentration fields for smoldering in an array of cylinders, for $X'_{F}=14$ (vertical marks), $\Delta=0.2175$ and $Pe_O = 2$, 5 and 10 [12]. The concentrations are the fuel content $c'_C$ in the grains and oxygen concentration $c'_O$ in the gas, normalized by their initial values. $T$ is normalized by the adiabatic temperature $T_{ad}$. Air is supplied from the left.

Figure 3. Temperature fields for smoldering in an array of cylinders, for $X'_{F}=14$ (vertical marks), $Pe_O = 10$ and various $\Delta$ [12]. Same color code as in Fig. 2.

Figure 4. Close-ups of the temperature fields in the reaction zone, in two cases from Fig. 3.
where $\varepsilon_g$ and $\varepsilon_s$ are the gas and solid volume fractions, $C_g$ and $C_s$ their volumetric heat capacities, $\Delta = \varepsilon_g \Delta c_g v^* / C U_F$ and $\Delta = \varepsilon_s C_g \Delta c_s + C U_F$ the concentrations of fuel and oxygen consumed in the process, generally equal to their initial amounts. It is also worth noting that $\Delta$ does not depend on the flow rate, nor on the heat release. It determines the global thermal behavior of the system, and first of all the reaction leading or trailing status of the process [13]. When $\Delta > 1$, most of the heat produced in the reaction zone is convected to the downstream side, where the temperature reaches a plateau $T_p$. Conversely, when $\Delta < 1$, most of the heat is left behind the progressing reaction zone, where temperature raises at the value $T_p$. This is illustrated in Fig. 3, where $\Delta$ is varied for a constant value of $PeO$. The plateau temperature is also determined by $\Delta$. In both cases,

$$T_p = T_{ad} / |1 - \Delta|$$

where $T_{ad}$ is the adiabatic temperature, resulting from the release of the heat of reaction in the solid material. Note that the range $0 < \Delta < 2$ yields a superadiabatic regime with $T_p > T_{ad}$. The particular case $\Delta = 1$ is degenerated and cannot yield a stationary regime.

The last parameter, $Pe_{F,s}$, is also a Péclet number, which compares the characteristic times $L^2/D_{F,s}$ for heat diffusion in the solid and $L/UF$ for the reaction front progress

$$Pe_{F,s} = U_F L / D_{F,s}$$

It tells whether the heat produced by the chemical reaction spreads in the solid faster than the front progresses, or whether thermal disequilibrium prevails in the solid in the reaction zone. It can also be felt that $Pe_{F,s}$ determines the width of the hot region around the reaction front, and controls in particular the preheating of the solid, with determinant influence on the viability of the smoldering process. Figure 4 provides an illustration, with two situations where local equilibrium is fullfilled ($Pe_{F,s} < 1$) or not ($Pe_{F,s} >> 1$). In the latter case, a mean solid temperature is clearly unrepresentative of the temperature at the reaction site, and its use in the kinetic laws is very questionable.

Hence, in the framework of this extremely simple chemical model, $Pe_{F,s}$ provides an a priori criterion for the validity of a local equilibrium hypothesis, and therefore for the applicability of standard homogenized formulations. This is possible because there are only two time scales involved, which are easy to evaluate. However, it will be seen in the following that more complex chemical schemes give raise to a variety of time scales, relative to the species transports and to the various chemical reactions. The latter depend non linearly on temperature, and it is very difficult to predict which are the limiting processes. The main interest of our local simulations, which give access to the local thermochemical parameters, is to allow to investigate these situations.

**Influence of the pyrolytic reactions**

Two kind of pyrolytic processes, which had not been considered in the first investigations, are taken into account here. The first one is the cracking of the kerogen ($K$) in the oil shale, which results in the emission of volatile species ($V$) and leaves the carbon char ($C$) that is later oxidized according to (1). It can be written in the generic form

$$K + \Delta H_p \rightarrow C + V$$

Since the parameters of (7) and even the exact nature of $K$ and $V$ are not well known, we used the results of the measurements of [5] in the simulations. In particular, [5] showed that this
reaction is nearly athermal ($\Delta H_c \approx 0$), and that it occurs when temperature exceeds a threshold $T_{r,p} \approx 200^\circ$C. Therefore, the kerogen which is initially present in the shale grains is progressively converted into char, when $T$ reaches $T_{r,p}$, at a rate which is limited by the conductive heat supply (until exhaustion of $K$). We do not keep track of the volatiles species in the simulations. They are a valuable product, and it is generally preferred to collect them at the outlet rather than burning them in the reactor. Hence, we try to determine under which conditions they can escape, but we do not investigate in details what would happen if they cannot.

The second pyrolytic reaction is the decarbonation of the mineral matrix material, and it has a more significant impact because of its strongly endothermal character. It can be written in the generic form

$$XCO_3 + \Delta H_c \rightarrow XO + CO_2$$

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\[
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\] (8)

Figure 5. Comparison of simulations with only the oxidative reaction $\{O\}$ and with calcination and craking $\{OCP\}$ in a layered material. PeO=10. Distances are normalized by the channel width $W$, and measured relative to the oxydation front $X_F$. First row: Mean temperature profiles, in natural and logarithm scales for the abscissa. Second row: species concentration profile, for $\{O\}$ (left) and $\{OCP\}$ (right). Third line: temperature, carbonate and kerogen concentration fields, for $\{OCP\}$. 

\[
T \quad \frac{[CaCO_3]}{[CaCO_3]_in} \quad \frac{[K]}{[K]_in}
\]
where $X$ stands for Ca or Mg since both types of carbonates exist in the shales. As the cracking, decarbonation is driven in the simulations by the conductive heat supply, when $T$ reaches a threshold $T_{r,c} = 750^\circ C$. It induces a significant thermal sink since $\Delta H_c$ was measured as 1540kJ/kg of carbonates [5]. Given the composition of the oil shales, full decarbonation could consume 41% (1.50 GJ/m$^3$) of the heat released by the complete char oxidation (3.63 GJ/m$^3$). From a global point of view, this results in a reduced apparent heat release for the reaction (1), from which modified (lower) values of $T_{ad}$ and $T_p$ can be deduced.

An illustration is provided in Fig. 5, for smoldering in a layered medium made of shale slabs separated by plane channels of aperture $W$. Longitudinal temperature profiles are shown, with or without accounting for the pyrolytic processes (cases referred to as {OCP} and {O}, respectively). As mentioned, {OCP} results in a lowering of $T$, by a factor corresponding to the lower net heat release. This is due to calcination only, the athermal cracking does not contribute to this effect. The upstream plateau at $T_p$ is clearly visible (since $\Delta = 0.38 > 1$), as well as the exponential decay on the downstream side of the front (slimlog plot on the right).

The concentration profiles for {O} involve only C, O$_2$ and CO$_2$. C is exhausted upstream of $X_F$, where CO$_2$ is produced. The oxygen concentration decays exponentially in the reaction zone. The plot for {OCP} shows additional curves for the kerogen and the carbonates. Since $T_{r,c}$ is rather low, cracking (i.e. conversion of K into C) occurs relatively far downstream of $X_F$, at a distance about 4.5$W$. This is also where the volatile species $V$ are released. Conversely, because $T_{r,c}$ is much higher, decarbonation takes place much closer to $X_F$. There is actually no separation between the oxidation and calcination zone.

In this case, there is a small amount (~1.5%) of O$_2$ remaining at the position of the cracking front. Since the volatile species are not explicitly considered here, this fraction of oxidizer escapes from the reactor. But in a real situation, V and O$_2$ could react if they come to meet, and depending on the operation conditions (for instance with larger $Pe_O$), it could involve a more significant fraction of the oxygen supply. The simplest way to avoid this is to shift the cracking front as far downstream of the oxidation front as possible. This can be achieved by keeping $T_p$ as large as possible, or by decreasing the decay rate of $T$ downstream of $X_F$, and shifting $\Delta$ toward unity serves both of these purposes.

Conversely, this illustrate the potentially negative effect of decreasing $\Delta$. This is generally done by mixing the shale with inert sand and it might be desirable from several other points of view, such as the reduction of NO$_x$ production, simplification of the reactor design, for safety and thermomechanical considerations, reduction of transverse heat losses, and limitation of the decarbonation. It will be seen in the next Section that lowering the temperature level may also strongly modify the chemical processes, and sometime induce massive CO emission.

The last row in Fig. 5 shows the local temperature, carbonate and kerogen concentration fields for {OCP}. Note that in this case the decarbonation is complete, because the net heat release yields then a value of $T_p$ which is still larger than $T_{r,c}$. If this were not the case, decarbonation would be only partial, to the degree which would yield $T_p = T_{r,c}$. It could even not occur at all, if $T_p$ does not reach $T_{r,c}$. It is possible, given the composition of the shale, to predict a priori the plateau temperature and the degree of calcination to be expected (see [10]).

**Improved oxidative reaction scheme**

The numerical simulator in its latest form includes a richer oxidative chemical model, which involves four species and three reactions.

\[
\begin{align*}
(R1) \quad & C + \frac{1}{2}O_2 \rightarrow CO \\
(R2) \quad & C + CO_2 \rightarrow 2 CO \\
(R3) \quad & CO + \frac{1}{2}O_2 \rightarrow CO_2
\end{align*}
\]
Direct oxidation of C into CO\textsubscript{2} is ruled out, because of the general consensus that it is negligible compared to reaction (R1), which was confirmed by our first simulations when it was included. The first two reactions are heterogeneous, while the latter is homogeneous and takes place in the gas phase. They are exothermic, except for the Boudouard reaction (R2), which is endothermal. Because it is much more important here than in the simpler scheme (1) to carefully account for the characteristic times of the various reactions, their kinetic laws are not schematized by bimodal models of the type of (2), but described by actual Arrhenius laws functions of the local temperature and concentrations and taken from the literature. There is however a puzzling degree of uncertainty regarding their parameters and in some instances adjustments had to be made in order to comply with physical realisms [10].

Figure 6 provides a schematic view of the chemical scheme. It is important to note that it is impossible to guess which reaction actually occurs and in which proportion from what is observable to the operator of the reactor, i.e. from the composition of the outgoing gas. This composition can be characterized by the fractions $\omega_{\text{O}}$ of escaping oxygen and $\omega_{\text{C}}$ of CO in the produced carbon oxides. This is illustrated by three totally different examples that yield the same products, with $\omega_{\text{O}} = \omega_{\text{C}} = 0$, i.e. the same result as reaction (1) which is not even present in the model.

In addition, the previous global predictions of $T_{\text{ad}}$, $T_{p}$, $U_{F}$ and the values of the criteria $\Delta$ and $P_{F,s}$ established in the case of a complete oxidation of C into CO\textsubscript{2} are not valid anymore, because the global stoichiometry is modified. For instance, the real parameter $\Delta_{r}$ is related to the nominal value $\Delta_{n}$ given by (4) by

$$\Delta_{r} = \frac{1 - \omega_{r} / 2}{1 - \omega_{\text{O}}} \Delta_{n}$$

\hspace{1cm} (10)

\textbf{Figure 6.} Global reaction scheme (top). The species fluxes and reaction rates are normalized by the oxygen supply rate. Three examples of different schemes which yield the same products (bottom)
It is therefore of practical importance to establish a phenomenological chart of the various behaviors associated with different operating conditions, and this was the first task addressed in [10]. Systematic calculations have been conducted with the simple geometrical model of a layered medium. A typology of regimes was identified, and criteria could be formulated. Simulations in the less simple network of cylinders confirmed the conclusions, although the transition between regimes are less sharp. This is due to a continuous range of length scales in the medium instead of a well defined single one. This is why we present here only results for the layered medium. Our data set is more complete, and it is more illustrative from a pedagogical point of view.

Let us start by considering a reference situation with $P_{eO} = 10$, $\Delta n = 0.38$. The global reaction scheme is similar to example (b) in Fig. 6. Nearly all the oxygen is consumed ($\omega_O = 0.004$) and the emission of monoxide is moderate ($\omega_C = 0.17$). The local results are displayed in Fig. 7. The macroscopic aspect of the temperature field is as expected, with the usual upstream plateau, but a very hot spot exists in the gas, which is of course not predicted when only the surface reaction (1) is implemented. It results from the secondary oxidation (R3), which is the most energetic one. CO is produced by (R1) at the entry of the reaction zone, and latter converted into CO$_2$ for its most part. However, CO$_2$ also reacts significantly with the char in the solid by Boudouard reaction. The couple of reactions (R2,R3) acts as a chemical pump of C, which contributes nearly as much as (R1) to the extraction of C from the shale.

The oxidation of CO in the gas occurs in a flame which settles at some distance from the solid walls as the result of a complex competition of times scales, for the chemical reactions and diffusion processes. Figure 8 shows two examples similar to Fig. 7 except that the air supply rate is twice smaller or twice larger. The global rate of (R3) does not change significantly, but the morphology of the flame changes from diffuse throughout the channel to thin and parietal. These two situations

![Image](image)

Figure 7. Temperature field (global view and zoom on the reaction zone), O$_2$, CO and CO$_2$ concentrations and rate of the homogeneous reaction (R3), in the reference case $P_{eO} = 10$, $\Delta n = 0.38$. 
should obviously be addressed by using different formulations in a macroscopic model. Meanwhile, the rate of CO emission also varies, and increases as the flow rate decreases, from $\omega_{C} = 0.11$ when $PeO=20$ to $\omega_{C} = 0.24$ when $PeO=5$. However, the most dramatic effect occurs when the flow rate is decreased further to $PeO=3$. The flame suddenly disappears, the rate of (R3) nearly vanishes, and CO is massively produced with $\omega_{C} = 0.80$. The same occurs if $\Delta n$ is slightly decreased from 0.38 to 0.35, which can be done by modifying the char content in the solid.

The transition between these two regimes, without of with a flame which we denote A and B, respectively, is reversible. When increasing again the flow rate of entering a region richer in fuel, the flame starts again spontaneously. Furthermore, all flameless regimes are associated with massive CO emission and oxygen escape rate. The transition between A and B depends mostly on the compositional parameter $\Delta n$, with only marginal influence of $PeO$. This could be partly substantiated and predictive criteria for the regime to be expected have been proposed [10].

Other regimes, associated with excursions along different directions from the reference situations, have been observed. A summary is shown in Fig. 9. Each case is associated with different kinds of global products, ranging from pure CO to pure CO$_2$.

**Figure 8.** Rate of the homogeneous reaction (R3), in the cases $PeO=5$ and 20, for $\Delta n=0.38$.

**Figure 9.** Summary of the regimes, for varying operating conditions.
Concluding remarks

Our numerical model has demonstrated its ability to handle complex chemical processes, on a microscopic scale and with a detailed account of the main coupling mechanisms responsible for the physicochemical behaviors. An extensive phenomenological survey of the various possible regimes has been conducted, which exhibits features potentially crucial for the operation of the reactor and for its macroscopic modelisation. Quantitative predictions are possible, although they are somewhat sullied by the uncertainty about the thermochemical parameters of the model.

One of the most desirable and important extensions is an account of the radiative heat transfers, which are ignored at this stage. It would somewhat regularize the local variations of temperature by allowing heat exchanges between non contacting solid bodies, and by providing an additional way for heat to be transferred from the hot spots in the gas, where $T$ sometimes reaches unphysically high values. This issue is currently being addressed, by using the same microscopic approach and the same level of detail [14].

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References