

Development of a model for the characterization of fluid dispersion in electrochemical reactors

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ABSTRACT

This paper analyses the hydrodynamic behaviour of electrochemical reactors by simulating stimulus–response experiments. The experiments were performed with a simple experimental arrangement to generate data (Residence Time Distribution (RTD) curves) from electrolytic conductivity measurements. The multiparametric model proposed and the Matlab program developed allow the study of electrochemical reactors using three-dimensional electrodes, providing values of characteristic parameters of the materials, such as porosity and compressibility. The study of the reactor also permits modelling of the electrochemical reactions that will be produced inside it.

Key words | characterization, electrochemical reactor, filterpress cell, hydrodynamics, mathematical model, RTD

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INTRODUCTION

Filter-press cells (Walsh 1993) are one of the most used reactor systems in electrochemical applications due to their many benefits. Their advantages can be seen from an industrial, research or practical point of view: wide availability of its components; ease of scale-up, versatility, which enables the electrolyzers to be used in different configurations for a wide variety of processes; growth in the successful application of pilot and full scale electrochemical filter-press reactors (Pletcher 1991); wide variety of commercial electrochemical filter-press reactors from laboratory to industrial scale; simplicity of construction; uniform potential distribution; ease of operation and minimal maintenance problems; possibility of electrical monopolar or bipolar connection; and incorporation of turbulence promoters and incorporation of three-dimensional electrodes (Ponce de Leon & Pletcher 1996).

The implementation of three-dimensional electrodes in electrochemical reactors provides an effective method for improving the efficiency of some electrochemical processes, such as wastewater treatment, electrosynthesis and energy storage. The increase in surface area due to the

high porosity of these materials is of special interest in diffusion–convection controlled processes. The flow distribution inside the reactor compartments is highly influenced by the characteristics of the porous material. It has been observed by Lopez de Atalaya (1991) that the ratio of felt thickness to cell thickness has an influence on the flow distribution, pumping power and electrode–contact losses. The general hydrodynamic behaviour of this kind of reactor is presented in Figure 1. Note that two different pathways inside the reactor are present. Other important aspects are noted in Figure 1.

This paper presents a model for the reactor and a program, written in Matlab 5, that optimizes the parameters of the model. The optimization includes the resolution of a system of two equations in partial derivatives. The conditions for the convergence of the system are discussed and implemented. The program is then used for the modelling of an experimental reactor, previously described by González-García *et al.* (2000), and the results are discussed. Recently, this program has been used for the modelling of an industrial size electrochemical reactor (Frias-Ferrer *et al.* 2001).

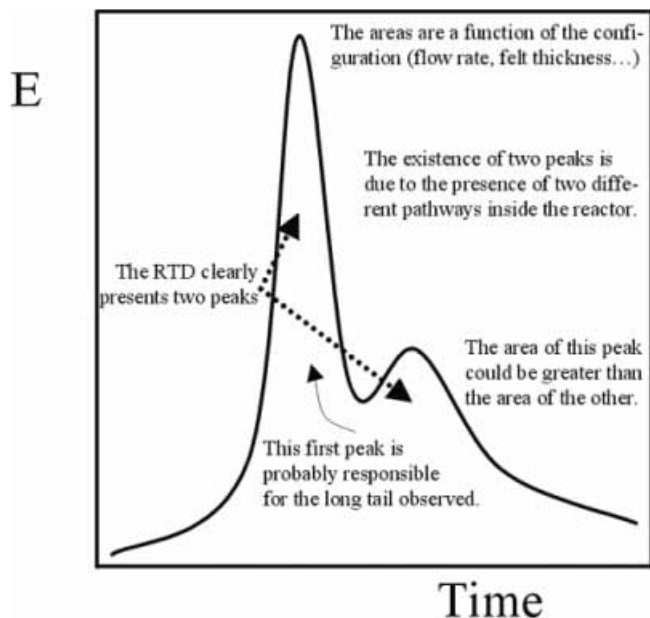


Figure 1 | Description of the curves.

MODELLING THE REACTOR: MASS BALANCE AND MODEL

Total mass and species mass balances

For any fluid, we require that the total mass flow into some element of volume minus the out flow is equal to the rate of accumulation of mass and we either write these as integral balances (stoichiometry) or as differential balances on a differential element of volume:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \quad (1)$$

where ρ is the density, and the term in bold italic is a vector with x , y and z coordinates, i.e. the velocity \mathbf{u} has three components. The usual forms of the balances are concerned with u_z , the velocity component in the direction of flow down the tube.

When we assume a steady-state density-constant reactor, we obtain the simple form of this equation:

$$(\rho u) = 0 \quad \text{or} \quad \rho u = \text{constant} \quad (2)$$

which is a statement of mass conservation, as required by stoichiometry.

This equation applies to the total mass density of the system, while we use the amount of material when describing any chemical reactions.

For a multicomponent fluid (the only case of interest for chemical reactions) we next have to solve the mass balance for each individual chemical species. The species balance is written as 'flow in' minus 'flow out' plus 'change due to chemical reaction' equals the 'accumulation of that species'. There is, of course, an equation for each species, subject to the conservation of total mass given by the continuity equation. The species balance equations are

$$\frac{\partial C_j}{\partial t} + \mathbf{u} \cdot \nabla C_j = D_j \nabla^2 C_j + \sum_{i=1}^R v_{ij} r_i \quad (3)$$

In the derivation of this equation we assume that the density is constant and the diffusivity D_j is independent of composition, and we simplify the convection term somewhat. ∇ and (∇^2) are the gradient and Laplacian operators, respectively.

For a tubular reactor, assuming variation in only one spatial dimension, the direction of flow z , we obtain

$$\frac{\partial C_j}{\partial t} + u \frac{\partial C_j}{\partial z} = D_j \frac{\partial^2 C_j}{\partial z^2} + \sum_{i=1}^R v_{ij} r_i \quad (4)$$

where u is the velocity in the direction of flow (the z direction), and all the gradients are assumed to be in the axial (not the radial) direction. The units of the last term represent the moles of the species per (metre)³ per second that leaves the reactor due to the chemical reaction.

Model of the reactor

The reactor considered in this work has been characterized using input tracer experiments to measure the residence time distribution (RTD). The form of this function is shown in Figure 1. To develop a model for the observed behaviour, different non-ideal flow models have been tested. These models are based on the combination of the dispersed plug-flow reactor and tank-in-series models. Levich *et al.* (1967) consider the hydrodynamic mixing in a

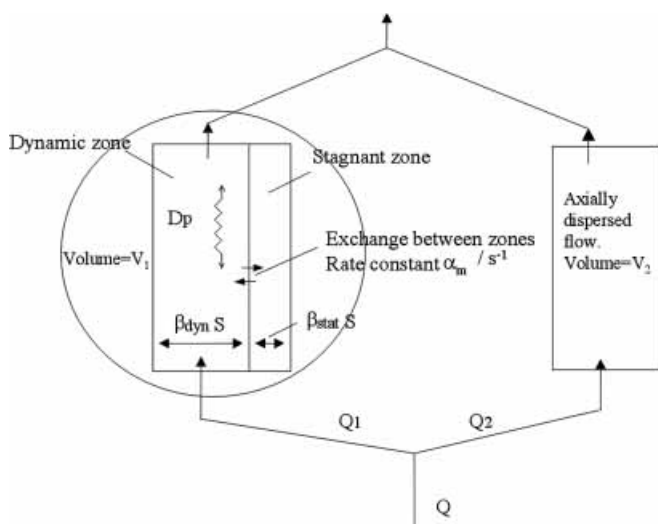


Figure 2 | Two pathways model.

porous medium with the help of a model containing a series of perfect mixers with stagnant areas, and studied the relationship between this model and the usual diffusional one. They concluded that the distribution (for a run with only one peak in the RTD) can be represented as the sum of two distributions (a normal distribution and an exponentially decaying one) and determined the parameters of the porous medium from the experimental results.

In our case, and due to the existence of two peaks in the RTD, the model proposed considers two possible paths along which the electrolyte may flow. A scheme of this model is shown in Figure 2.

For one of the paths (path 1, occupying a volume V_1) it is assumed that the electrolyte flows according to a dispersed plug-flow model. It is also assumed that the volume V_1 is partially occupied by a stagnant area. The electrolyte in the stagnant areas is slowly refreshed by the freely flowing electrolyte that can be considered as an axially dispersed plug flow. The electrolyte hold-up in this zone, $\beta_{tot} = m^3(\text{liquid})/m^3(\text{column})$, is divided into a dynamic hold-up, β_{dyn} and a static or stagnant hold-up, β_{stat} (see Figure 2). The local rate of exchange between the dynamic (d) and static (s) hold-up is assumed to be proportional to the concentration difference in the dynamic and static phases, and it can be characterized by an exchange

coefficient, α_m (s^{-1}), defined by

$$\frac{\text{number of moles exchanged}}{m^3(\text{liquid}) \cdot s} \equiv \alpha_m (c_d - c_s) \quad (5)$$

where c_d and c_s are the concentrations in the dynamic and static phase respectively. α_m can be considered as the product of a mass transfer coefficient and the specific interfacial area between the flowing and the stagnant zones, $k_L a$.

The model equations can be found by applying the mass balance equation (4) to the dynamic and the static phases over a thin slice perpendicular to the direction of the flow. We assume the density and other variables to be constant over the length of the reactor:

$$\beta_{dyn} S \frac{\partial c_d}{\partial t} = \beta_{dyn} S D_d \frac{\partial^2 c_d}{\partial z^2} - \beta_{dyn} S u_d \frac{\partial c_d}{\partial z} - \beta_{tot} S \alpha_m (c_d - c_s) \quad (6)$$

$$\beta_{stat} S \frac{\partial c_s}{\partial t} = -\beta_{tot} S \alpha_m (c_d - c_s) \quad (7)$$

where S = cross sectional area of the reactor (m^2); D_d = dispersion coefficient in dynamic phase ($m^2 s^{-1}$); u_d = velocity in the dynamic phase ($m s^{-1}$) of volume $V_1 = Q_1 / S \beta_{dyn}$ and Q_1 = electrolyte flow through volume V_1 ($m^3 s^{-1}$).

If we introduce some dimensionless units, we find from Eqs (6) and (7)

$$\Theta_B \frac{\partial C_d}{\partial \theta} = \frac{1}{Pe_d} \frac{\partial^2 C_d}{\partial Z^2} - \frac{\partial C_d}{\partial Z} - N_\alpha (C_d - C_s) \quad (8)$$

$$(1 - \Theta_B) \frac{\partial C_s}{\partial \theta} = -N_\alpha (C_s - C_d) \quad (9)$$

where $Z = z/L$, with L being the total length of the reactor; $\Theta_B = \beta_{dyn}/\beta_{tot}$; $N_\alpha = (\alpha_m L)/(\Theta_B u_1)$; $Pe_d = (u_1 L)/D_d$; $\theta = t/\tau$, with $\tau = L/(\Theta_B u_1)$; $C_s = c_s/c$ and $C_d = c_d/c$. In this way, N_α is the number of mass transfer units for the mass exchange between the dynamic and the static phase, and Pe_d is the Peclet number for the dynamic phase. For the calculation of the RTD due to this pathway, we will solve the pair of Eqs (8) and (9) with the appropriate boundary conditions.

For the other path (path 2, occupying a volume V_2), the dispersed plug-flow model, assuming a small dispersion grade, is applied. The curve representing the distribution of residence times for path 2 (E_2) (Levenspiel 1999) is

$$E_2 = \frac{1}{2\sqrt{\frac{\pi}{Pe_2}}} \exp\left(-\frac{\left(1 - \frac{t}{\tau_2}\right)^2}{\frac{4}{Pe_2}}\right). \quad (10)$$

In this equation, Pe_2 is the Peclet number for path 2, t is the time from the injection of a tracer and τ_2 is the mean residence time for path 2.

Considering that the model proposed for path 1 may be applied to a volume V_1 that has a flow rate Q_1 , and the model for path 2 may be applied to a volume V_2 , with a flow rate Q_2 , we write

$$V_{\text{tot}} = V_1 + V_2 \quad (11)$$

$$Q = Q_1 + Q_2 \quad (12)$$

and the mean residence times will be given by the equations

$$\tau_i = V_i/Q_i \quad i = 1, 2. \quad (13)$$

The total RTD is calculated using the following equation (Levenspiel 1999):

$$E = E_1 \frac{Q_1}{Q} + E_2 \frac{Q_2}{Q}. \quad (14)$$

For the evaluation of the parameters, an objective function is defined:

$$\text{OF} = \sum_r \sum_k (E_{k,\text{cal}} - E_{k,\text{exp}})^2. \quad (15)$$

In this equation, r represents each experiment at a different flow rate, k represents the data collected at each time, and the sub-indexes 'cal' and 'exp' correspond to the calculated and experimental data, respectively.

The values that must be optimized are: τ_1 , Θ_B , Pe_d , N_α , τ_2 and Pe_2 . Note that the minimum number of parameters

is used, using expressions such as Eq. (13) (i.e. the volume and the flow rate are not optimized, because there is a known relationship between them).

SOLUTION OF THE SYSTEM OF PARTIAL DIFFERENTIAL EQUATIONS

In the program the method used to solve the system of equations is the finite difference method (Finlayson 1980). If we develop Eq. (9) in terms of this method, we find

$$(1 - \Theta_B) \frac{C_{s,i}^{t+1} - C_{s,i}^t}{\Delta\theta} = -N_\alpha (C_{s,i}^t - C_{d,i}^t) \quad (16)$$

and rearranging:

$$C_{s,i}^{t+1} = \left(1 - \frac{N_\alpha \Delta\theta}{1 - \Theta_B}\right) C_{s,i}^t + \frac{N_\alpha \Delta\theta}{1 - \Theta_B} C_{d,i}^t. \quad (17)$$

For Eq. (8), following the same procedure, it is found that

$$\begin{aligned} C_{d,i}^{t+1} &= C_{d,i+1}^t \left[\left(\frac{\Delta\theta}{Pe_d \Theta_B (\Delta z)^2} \right) - \frac{\Delta\theta}{\Theta_B \Delta z} \right] + \\ &C_{d,i}^t \left[\frac{-2\Delta\theta}{Pe_d \Theta_B (\Delta z)^2} + \frac{\Delta\theta}{\Theta_B \Delta z} - \frac{N_\alpha \Delta\theta}{\Theta_B} + 1 \right] + \\ &C_{d,i-1}^t \left[\frac{\Delta\theta}{Pe_d \Theta_B (\Delta z)^2} \right] + \frac{N_\alpha \Delta\theta}{\Theta_B} C_{s,i}^t. \end{aligned} \quad (18)$$

To study the stability of the equations we can use the following theorem (Finlayson 1980):

If $C_i^{t+1} = AC_{i+1}^t + BC_i^t + DC_{i-1}^t$ and A, B, D are positive and $A + B + D \leq 1$, then the scheme is stable and the errors become negligible.	(19)
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Applying the theorem to Eq. (18), we found that, if $A > 0$, then

$$\Delta z < \frac{1}{Pe_d} \quad \equiv \text{Condition 1}$$

and if $B > 0$ then

$$\Delta\theta < \frac{\Theta_B \Delta z}{\frac{2}{Pe_d \Delta z} - 1 + N_\alpha \Delta z} \quad \equiv \text{Condition 2}$$

Bearing in mind Condition 1, Condition 2 results in

$$\frac{2}{Pe_d \Delta z} > 2.$$

This expression is always true if the product $Pe_d \Delta z$ is positive. The other two conditions, $D > 0$ and $(A + B + D) \leq 1$, are always true for Eq. (18).

Let us now develop the conditions for Eq. (17) to be stable. In this case, the most restrictive condition is when $B > 0$, i.e.

$$\left(1 - \frac{N_\alpha \Delta\theta}{1 - \Theta_B}\right) > 0 \quad \equiv \text{Condition 3.}$$

Rearranging we find

$$\Delta\theta < \frac{1 - \Theta_B}{N_\alpha} \quad \equiv \text{Condition 3.}$$

So, for the system of differential equations to be stable, we will need to compare the time increments given by Conditions 2 and 3, and choose the lower one.

Boundary conditions for the partial differential equations

For a 'closed' reactor (i.e. when a portion of fluid that enters the reactor cannot leave it by the same way), consideration of flux balances at the entrance and at the exit provide what are usually termed the 'Danckwerts boundary conditions' (Danckwerts 1958):

$$C_{A0} = C_A(0^+) - \frac{D}{u} \frac{\partial C_A(0^+)}{\partial z} \quad (20)$$

where C_{A0} is the input concentration of species A and the point 0^+ represents the first differential point inside the reactor. If we apply Eq. (20) to our case, we have

$$C_{d,i}^t = C_{d,i+1}^t - \frac{D_d}{u_d} \frac{C_{d,i+2}^t - C_{d,i+1}^t}{\Delta z} \quad (21)$$

Rearrangement gives

$$C_{d,i+1}^t = \frac{C_{d,i}^t Pe_d \Delta z + C_{d,i+2}^t}{Pe_d \Delta z + 1} \quad (22)$$

For the calculation of the E curve (or RTD curve), an input signal as a step experiment is considered:

$$\left. \begin{array}{l} \text{concentration} = 0 \quad \text{if } t < 0 \\ \text{concentration} = 1 \quad \text{if } t \geq 0. \end{array} \right\}$$

This would give the so-called F curve, related to the E curve by the relationship given in Levenspiel (1999):

$$F = \int_0^t E dt \quad \Rightarrow \quad E = \frac{dF}{dt} \quad (23)$$

In this way, the input signal used in the calculations is a step function that is later differentiated to obtain the E curve. The reason for this is the simplicity of the step boundary condition, compared to the pulse input.

The equation system proposed before has been solved by Villiermaux & Van Swaaij (1969) using the Laplace transformation. Due to the complexity of an analytical solution, the equation system has been solved numerically in this paper.

STRUCTURE OF THE PROGRAMS

For the purpose of this paper, two Matlab programs are used. These are, on the one hand, the main module (OPTIMISE.M), and, on the other, the function module (OBJECTIVE.M). The code of the programs is given at the end of the paper. A flow chart of the program is given in Figure 3.

In the main module, the experimental data is read, and the order to minimize the objective function is given. Also initial values of the six parameters are given. The calculation loop includes orders to save the calculated data every 75 iterations. Two files are generated, the first containing the experimental time, the experimental and calculated values of E , and the second file containing the optimized parameters.

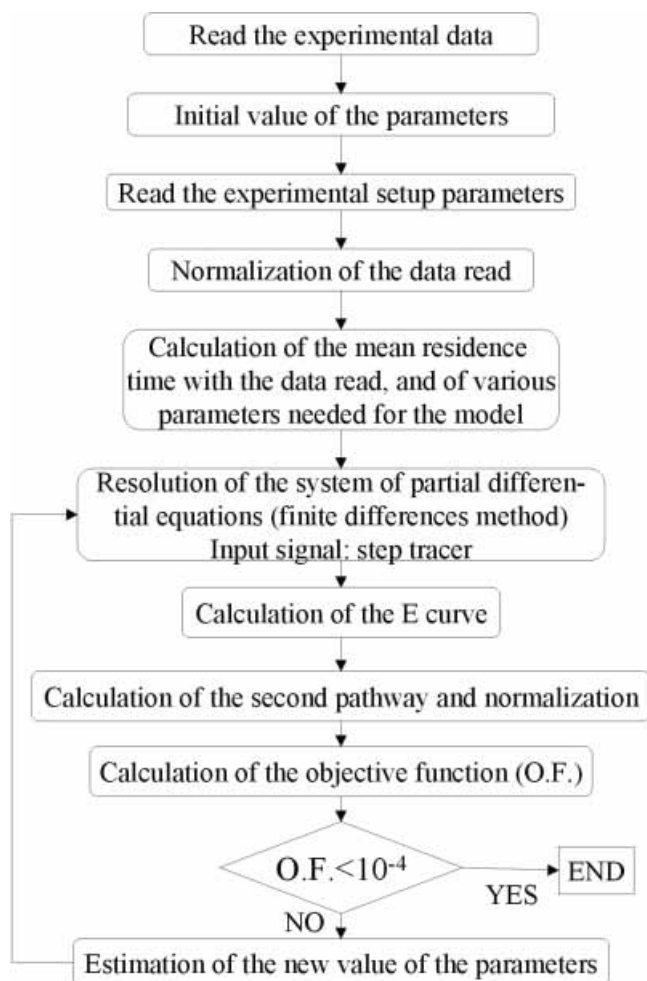


Figure 3 | Flow chart of the Matlab program.

The module with the objective function begins with reading the experimental set-up variables (flow rate, volume of the reactor, etc.). The next lines in the program calculate the experimental mean residence time (= volume/flow rate) and the mean time obtained from the experimental E curve, i.e.

$$\tau = \int_0^{\infty} E t dt \quad (24)$$

with the purpose of comparing them, in order to prevent possible errors.

The calculation begins with the parameters that the main module considers. The next step is to solve the

system of partial differential equations. The values of time increment and position increment are selected according to the conditions presented before.

At this point in the program, the conditions for the step experiment are introduced, and later the derivative will be calculated, in order to obtain the E curve. The program continues by applying the finite difference method for the resolution of the equations. It is possible to plot the concentration of the species versus the length of the reactor in each iteration, as we see in the codes, but this considerably slows the calculation.

The calculation of the contribution of the second pathway and the sum with the first are quite simple, considering the simple form of Eqs (10) and (14).

The problem now is that the E is calculated at times that do not match the experimental ones, so we must find the E values at the times that we have experimental data for, in order to compare them using Eq. (15). Interpolating at the times we have data, as explained in the program, solves this situation.

The program plots the results of E versus time, calculated and experimental, in order to have a visualization of the fitting in each iteration. If we would like to speed the calculation up, we must eliminate these lines in the program.

Finally the objective function is calculated and returned to the main module.

APPLICATION TO AN EXPERIMENTAL REACTOR

As an example, the programs described have been applied to the reactor UA200.08 implemented with carbon felt RVC 4002 (Le Carbon Lorraine). The properties of the reactor are described elsewhere (González-García *et al.* 2000). The runs considered here are performed at a flow rate of 33 L h^{-1} and using a cell thickness of 8 mm (Figure 4), whereas the carbon felt thicknesses were 8, 9, 10 and 13 mm. Taking into account the thickness of the cell, a felt thickness value of less than 8 mm would not produce a good electrical contact. On the other hand, a felt thickness above 13 mm would produce a very high-pressure drop, so it is not economically viable.

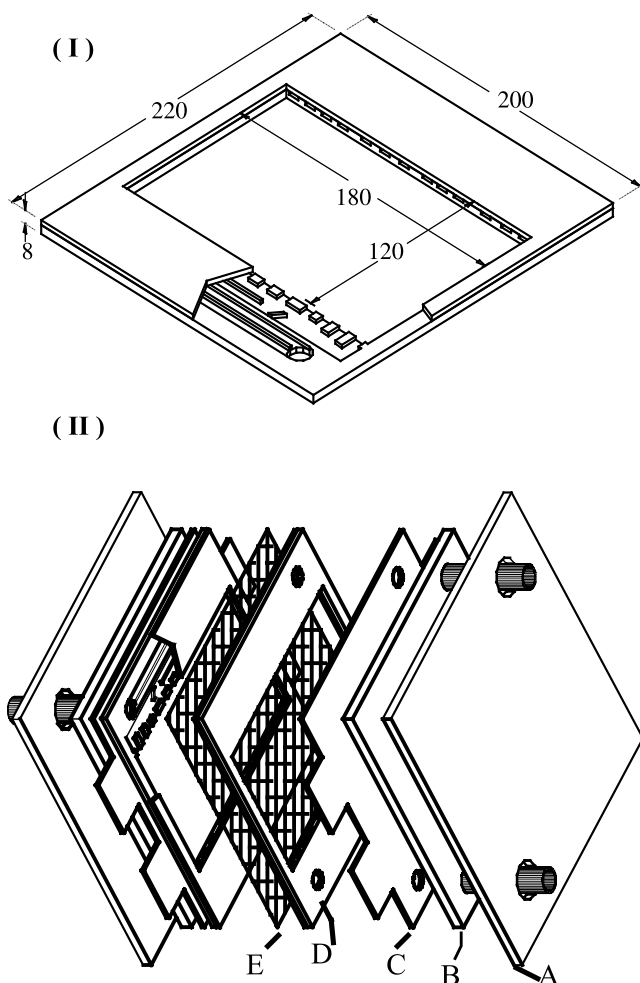


Figure 4 | (I) View of compartment (or chamber) showing details of flow distributors and geometric dimensions, in mm. (II) Exploded view of the UA200.08 reactor in the divided mode showing (a) backplate, (b) polypropylene block with flow channels, (c) flat plate, (d) compartment (or chamber), (e) separator.

Figures 5–8 show the experimental and calculated RTD curves obtained by the injection of a maker pulse of KCl at the inlet of the reactor accompanied by detection of the solution conductivity at the outlet (Harrel & Perona 1968) for ratios of felt thickness/cell thickness equal to 8/8, 9/8, 10/8 and 13/8. In the figures we can also see the contribution of each of the pathways inside the reactor to the total residence time distribution. As we can see, the fitting of the experimental data is satisfactory, except maybe in the long tail present in some curves. The fitting in this zone could be improved by modifying the objective function appropriately, for example increasing the relative

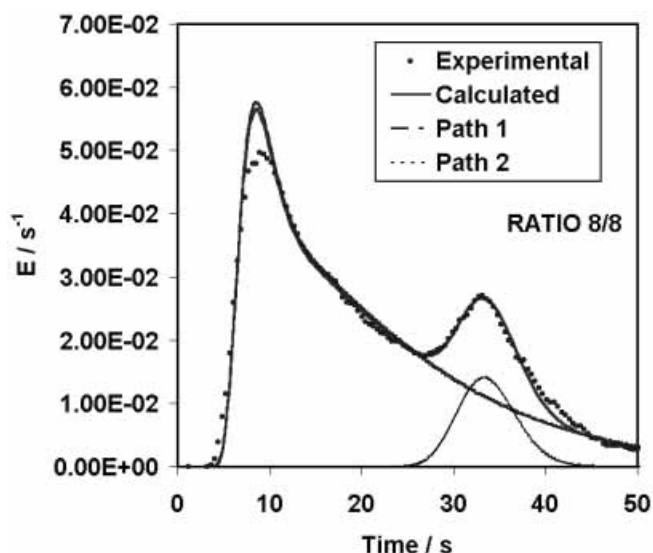


Figure 5 | Experimental and calculated curves for the 8/8 configuration.

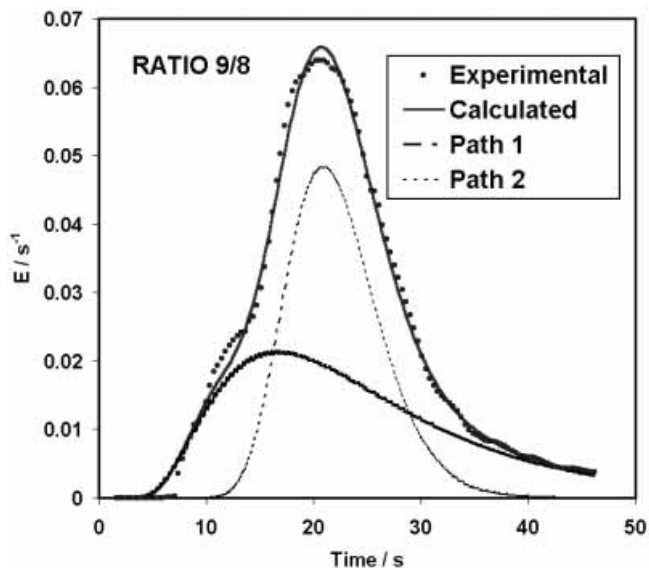


Figure 6 | Experimental and calculated curves for the 9/8 configuration.

weights of the differences in this zone, but a fit of these characteristics will not represent the whole experimental data.

The fitting parameters are presented in Table 1. Some other variables, calculated from the parameters fitted, are also presented in the table. It is important to note that all the calculated parameters have a useful and clear physical

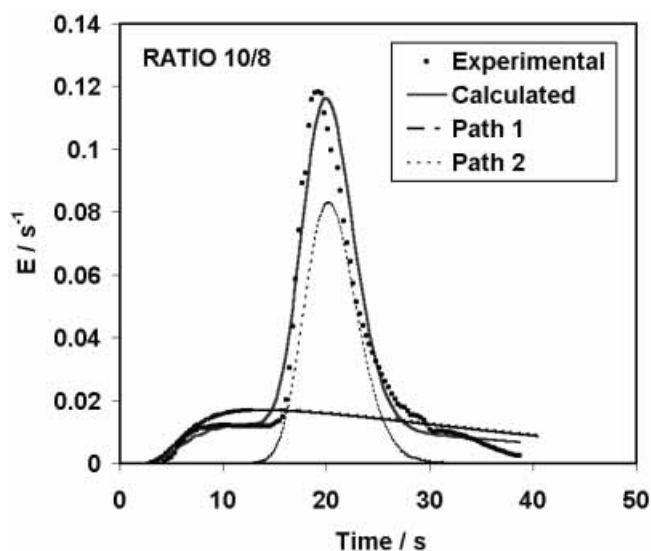


Figure 7 | Experimental and calculated curves for the 10/8 configuration.

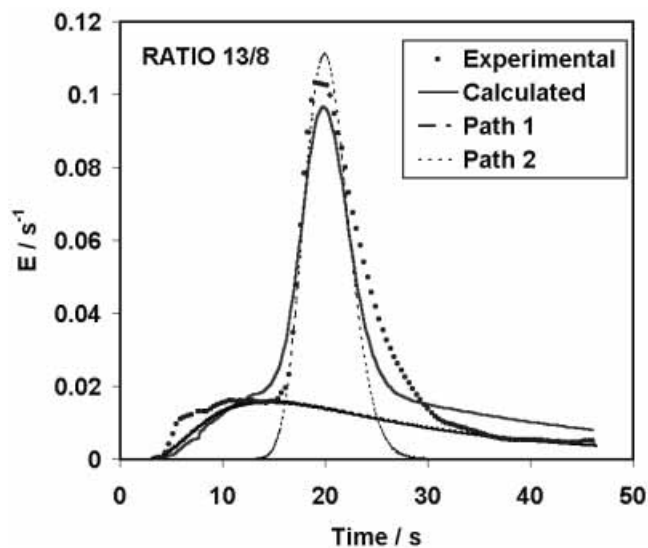


Figure 8 | Experimental and calculated curves for the 13/8 configuration.

meaning from the point of view of reactor characterization. The values of Pe and τ_i provide a clear statement of the hydrodynamic behaviour of the reactor. The ratio between the flow rates in each pathway is also illustrative of the reactor hydrodynamics. The values of β_{tot} are quite useful, because this parameter could be considered as the felt porosity. The porosity is quite easy to measure in rigid

Table 1 | Parameters of the fit and calculated variables

	Ratio	8/8	9/8	10/8	13/8
Parameters	τ_1 (s)	20.9	37.4	37.9	46.1
	τ_2 (s)	33.8	21.5	19.3	20.0
	Pe_d	20.1	5.6	4.4	2.5
	Pe_2	227.5	47.6	260.0	134.4
	Θ_B	0.4431	0.8455	0.8254	0.9137
Calculated variables	N_a	1.66	1.37	4.37	0.21
	β_{dyn}	0.4359	0.7149	0.8052	0.8866
	β_{tot}	0.9838	0.9800	0.9755	0.9703
	Q_1/Q	0.89	0.49	0.48	0.40
	Q_2/Q	0.11	0.51	0.52	0.60

porous media, but presents a great complexity to measure in materials such as felt, so the calculation describes a very good way to estimate it. The values obtained in the simulation of the RTD are in accordance with those proposed in the literature.

CONCLUSIONS

A model for a continuous flowing reactor has been developed that allows the characterization of the hydrodynamics. Mathematical development has been described in detail, from the total mass and species mass balances to the differential equations governing the behaviour of our particular reactor. There is a controversy between researchers relating to the use of multi-parameter models due to the loss of physical meaning in the parameters. However, in some cases, such as the present paper, the use of a multi-parameter model is fully justified since it gives information about physical properties that are difficult to obtain by other methods. This is the case of the parameter

β_{tot} that may be correlated with the felt porosity and these values of β_{tot} may be compared with other values obtained by other methods (González-García *et al.* 1999).

The program developed is a useful tool to study and characterize chemical reactors. Apart from identifying the number of possible pathways and quantify their proportion, the program can also be used to determine the value of the porosity of the medium. Nevertheless, the program cannot identify the nature of the different pathways, so it is not possible to affirm if the different pathways are physically separated, or, in contrast, if the liquid presents sub-layers close to the micro-skeleton of the material that retard the flowing of the liquid.

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NOTATION

a	Specific interfacial area between the flowing and stagnant zones, m^{-1} .
c	Concentration, mol m^{-3} .
c_d	Concentration in dynamic phase for path 1, mol m^{-3} .
c_s	Concentration in static phase for path 1, mol m^{-3} .
C_d	Normalized concentration in dynamic phase for path 1.
C_s	Normalized concentration in static phase for path.
D_d	Dispersion coefficient in dynamic phase, $\text{m}^2 \text{s}^{-1}$.
E_1	Residence time distribution (RTD) for path 1 (s^{-1}).
E_2	Residence time distribution (RTD) for path 2 (s^{-1}).
k_L	Mass transfer coefficient, m s^{-1} .

L	Length of the compartment in the direction of flow, m.
Pe	Peclet number, dimensionless.
Pe_d	Peclet number for path 1, dimensionless.
Pe_2	Peclet number for path 2, dimensionless.
Q	Volumetric flow rate, $\text{m}^3 \text{s}^{-1}$.
Q_1	Volumetric flow rate through path 1, $\text{m}^3 \text{s}^{-1}$.
Q_2	Volumetric flow rate through path 2, $\text{m}^3 \text{s}^{-1}$.
r	Rate of the reaction, $\text{mol m}^{-3} \text{s}^{-1}$.
S	Cross sectional area of volume 1, m^2 .
t	Time, s.
\mathbf{u}	Vector of velocities, m s^{-1} .
u_1	Lineal flow rate for path 1, m s^{-1} .
V_1	Volume of reactor for path 1, m^3 .
V_2	Volume of reactor for path 2, m^3 .
V_{tot}	Total volume of reactor, m^3 .
z	Coordinate in the direction of flow, m.
Z	Normalized coordinate in the direction of flow.

Greek letters

α_m	Exchange coefficient between dynamic and static hold-up for path 1, s^{-1} .
Θ_B	Fraction of dynamic zone for path 1.
β_{tot}	Liquid hold-up for path 1.
β_{dyn}	Dynamic hold-up for path 1.
β_{stat}	Static hold-up for path 1.
ν_{ij}	Stoichiometric coefficients.
θ	Dimensionless time.
τ	Averaged residence time, s.
τ_1	Averaged residence time for path 1, s.
τ_2	Averaged residence time for path 2, s.
∇	Gradient operator.
∇^2	Laplacian operator.

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PROGRAMS

Main module: OPTIMISE.M

```
%PARAMETERS: TAU1, THETA-B, PED, NA, TAU2, PE2
global fichero % Definition of global variables
load('c:\juan\eq\pb700b.txt'); % Reading the experimental data
% pb700b(:,1)==time
% pb700b(:,2)==experimental RTD
fichero=pb700b; % Renaming the variables containing experimental data

global fichero objectivefunction commontime eexp ecal % Definition of global
% variables

Contador=0 % Counts the number of iterations
Yousave=0 % Indicates if the program must save the results

Initial=[40 8.7756e-001 1.1240e+001 1.0023e+000 15 3.7533e+001] %Initial
values of the parameters shown in the first line

while funcionobjetivo>1e-4 | contador<500; %Begins the calculation loop

opciones(1)=1; % Options of the Matlab function FMINS. Option(1)=1
% means show the intermediate calculations
opciones(2)=1e-6; %==termination tolerance for the input vector
opciones(3)=1e-6; %==termination tolerance on function
opciones(14)=75; %==maximum number of iterations before saving
```

```
minimise=fmins('objetivo',Inicial, opciones) %Minimization of the
% function. The final results will be stored in a variable called
% 'minimise'

if contador==Yousave; %The program periodically saves the results
filetosave=[commontime(:,1) eexp(:,1) ecal(:,1)]
    save general.txt filetosave -ascii
    save optima.txt minimise -ascii;
% The file 'general.txt' will contain the time and experimental and
% calculated values of the RTD. The file 'optima.txt' will contain the
% best parameters for the optimization.
Yousave=Yousave +1;
end

Inicial=minimise;
contador=contador+1;
end

% End of the program
save general.txt filetosave -ascii
save optima.txt minimise -ascii;
pause
```

Function module: OBJECTIVE.M

```
function objectivefunction=objective(X) %definition of the function
global fichero objectivefunction commontime eexp ecal % Definition of global
% variables

% EXPERIMENTAL SETUP:
flowrate=(583/1000)*(1/3600); % Experimental value of the flow rate
ancho=18/100; % Dimensions of the reactor
alto=12/100; % Dimensions of the reactor
largo=0.8/100; % Dimensions of the reactor
volume=ancho*alto*largo; % Volume in m3
tresid=volume/flowrate; % Experimental residence time(s)
final=length(fichero); % Number of time intervals

% NORMALIZATION OF THE DATA READ:
integral=trapz(fichero(:,1),fichero(:,2)); % Integrates using trapezoid method
fichero(:,2)=fichero(:,2)/integral; % Experimental E normalized
finalt=fichero(length(fichero),1); % Final time in 'fichero'
```

```

% CALCULATION OF THE MEAN RESIDENCE TIME WITH THE DATA READ:
Ct=fichero(:,2).*fichero(:,1);
integraCdt=trapz(fichero(:,1),Ct);
tresidcurva=integraCdt;

% VALUES OF THE PARAMETERS:
% X=vector of values of the parameters that are used in each calculation
Tau1=X(1), % Renaming the variables
TB=X(2), if TB>1; TB=0.999; elseif TB<0; TB=0.01;end % No physical
% meaning of values of theta-b higher than 1
Ped=X(3), % Renaming the variables. Peclet number of dynamic phase
Nalfa=X(4), if Na<0, Nalfa=0.01; end % No physical meaning of values
% of Na minor than zero
Tau2=X(5), % Renaming the variables. Mean residence time path 2
Pe2=X(6), % Renaming the variables. Peclet number of path 2

% CALCULATION OF VARIOUS PARAMETERS NEEDED FOR THE MODEL
Btot=Tau1*flowrate/volume;
Bdyn=Btot*TB;
Velocd=caudal/(largo*ancho*Bdyn); % Lineal velocity in dynamic phase
Flow1=(volume-Tau2*flowrate)/(Tau1-Tau2); % Flow rate through path 1
Flow2=flowrate-Flow1; % Flow rate through path 2
Volume1=Tau1*Flow1; % Volume of path 1
Volume2=Tau2*Flow2; % Volume of path 2
Alpha=Na*TB*Velocd/alto;

% RESOLUTION OF THE SYSTEM OF PARTIAL DIFFERENTIAL EQUATIONS:
% 'F' CURVE. PATH 1=PATH 1=PATH 1=PATH 1

tf=finalt/Tau1; % Dimensionless final time
N=max([round(1.5*Ped),20]); % Number of position increments for each
% time calculation. It is selected the maximum between 1.5 times the
% Peclet number and 20. This value is partially due to Condition 1
% (see the text for more details)
incx=1/N; % Position increment, value given by Condition 1

inctiA=tb*incx/(2/(Ped*incx)-1+Na*incx); % Time increment as
% calculated following Condition 2 (stability of the first eq.)
inctiB=(1-tb)/Na; % Time increment as calculated following Condition 3
incti=min([inctiA, inctiB]); % Selection of the minimum

%Initial values of the concentration in dynamic and static zones:
Cd(1:N+1)=zeros(size(1:N+1)); % Dynamic phase conc. at a given time t
Cda(1:N+1)=zeros(size(1:N+1)); % Dynamic phase conc. at a given (t-1)

```

```

Cs(1:N+1)=zeros(size(1:N+1)); % Static phase conc. at a given time t
Csa(1:N+1)=zeros(size(1:N+1)); % Dynamic phase conc. at a given (t-1)

Cdo=1; %Initial value of the concentration in the dynamic phase at t=0
% and the inlet of the reactor (step experiment)
Cs(1)=0; % Initial value of the concentration in the static phase

Cd(1)=(Cdo*Pe*incx+Cd(2))/(Pe*incx+1); % The inlet value is affected by
% the flux. Application of Danckwerts boundary condition

% CALCULATION- FINITE DIFFERENCES METHOD
fCd=[ ];
fCs=[ ];
t=[ ];
ecall=[ ];
ecal2=[ ];
ecal=[ ];
time=0;

while time<tf
    time=time+incti;
    i=2;
    while i<N+1
        A=incti/(Pe*tb*incx^2)-incti/(tb*incx);
        B=-2*incti/(Pe*tb*incx^2)+incti/(tb*incx)-Na*incti/tb+1;
        D=incti/(Pe*tb*incx^2);
        Cda(i)=A*Cd(i+1)+B*Cd(i)+D*Cd(i-1)+Na*incti/tb*Cs(i);

        k1=-Na/(1-tb)*(Cs(i)-Cda(i))*incti; % Runge-Kutta 1st constant
        k2=-Na/(1-tb)*(Cs(i)+k1/2 -Cda(i))*incti; % Runge-Kutta
        k3=-Na/(1-tb)*(Cs(i)+k2/2 -Cda(i))*incti; % Runge-Kutta
        k4=-Na/(1-tb)*(Cs(i)+k3 -Cda(i))*incti; % Runge-Kutta
        Csa(i)=Cs(i)+1/6*(k1+2*k2+2*k3+k4); % Conc. Increment
        i=i+1;
    end

    Cd=Cda;
    Cs=Csa;
    fCd=[fCd,Cd(N)]; % fCd vector=saves the values of concentration
    % in dynamic phase at the exit of the reactor
    fCs=[fCs,Cs(N)]; % fCs vector=saves the values of concentration
    % in static phase at the exit of the reactor
    t=[t,time];

```



```

Cd(1) = (Cdo*Pe*incx+Cd(2)) / (Pe*incx+1);
Cs(1) = 0;
Cd(N+1) = Cd(N);
Cs(N+1) = Cs(N);

% The next four lines draw Cs and Cd in the reactor at each time, and
% are with a '%' for calculation purposes
% x=linspace(0,1,N);
% plot(x,Cd(1:N),x,Cs(1:N))
% axis([0,1,0,1])
% drawnow

end

% CALCULATION OF THE 'E' CURVE FROM THE 'F' CURVE:
ecal1=diff(fCd)./diff(t); % Differentiates numerically
ecal1=[ecal1 0]; % The last point that is not calculated

% CALCULATION OF THE SECOND PATH WAY
% 'E' CURVE. PATH 2=PATH 2=PATH 2=PATH 2

time=0;
i=1;
while time<tf
    time=time+incti;
    time2=time*Tau1/Tau2; % Dimensionless time for path 2. The number of time
    intervals has to be the same that with path 1.
    ecal2(i)=1/(2*(3.1416*time2/Pe2)*0.5)*exp(-(1-time2)*2/(4*time2/Pe2));
    % Equation that defines the RTD
    i=i+1;
end

% Normalization of the calculated curves:
integrall1=trapz(t,ecal1);
integral2=trapz(t,ecal2);
ecal1=ecal1/integrall1;
ecal2=ecal2/integral2;

% Adding the two contributions:
ecal=(ecal1'.*Flow1+ecal2'.*Flow2)./flowrate;
% This 'ecal' is calculated at times that do not match the
% experimental ones, so we must find the 'ecal' values at the times
% that we have experimental data, in order to compare.

```

```
commontime=t*Tau1;
ecalready=interp1(commontime,ecal,fichero(:,1)'); % Interpolates the
% vectors 'ecal' and 'fichero(:,1)' at the times given by 'commontime'
eexp=fichero(2:final,2);
ecal=ecalready(2:final)';

otrav=abs(eexp-ecal); % Differences between experimental and calculated
% values of the 'E' curve.

objectivefunction=sum(otrav) % Objective function

% PLOTTING THE RESULTS:
figure(1)
plot(commontime,eexp,'--',commontime,ecal);
drawnow
```