Teaching Residence Time Distributions in the Laboratory*

J. M. LOPES, F. LEMOS, C. PINHEIRO, F. RAMÔA RIBEIRO
*Instituto Superior Técnico,Dep. Engenharia Química, Av. Rovisco Pais, 1049-001 Lisboa, Portugal.
E-mail: jmlopes@popsrv.ist.utl.pt*

F. D. MAGALHÃES, A. MENDES, C. COSTA
Faculdade de Engenharia da Universidade do Porto, Portugal

This article describes the approaches that have been used in the laboratory teaching of Residence Time Distribution (RTD) analysis for the study of chemical reactors, in the Chemical Engineering courses at Instituto Superior Técnico—Universidade Técnica de Lisboa (IST) and at Faculdade de Engenharia—Universidade do Porto (FEUP). An integrated set of experiments has been used to allow the students to test the fundamental knowledge and to analyze working reactors. This involves determining RTDs, both by impulse and step tracer injection techniques, and applying them to the modeling of the reactor flow and to the estimation of the behavior of a non-linear chemical transformation. Very simple forms of obtaining non-ideal reactor behavior are used, such as deficient agitation in continuous stirred tank reactors. Continuous tubular reactors were manufactured so as to present axially dispersed plug flow and laminar flow.

INTRODUCTION

CHEMICAL REACTORS are very important pieces of equipment in any chemical industry facility. Undergraduate chemical engineering laboratories should then address chemical reactor experiments [1, 2]. In some cases the ideal reactor approach of the piston flow pattern for Tubular Reactors (PFR) or perfect mixing pattern for Continuous Stirred Tank Reactors (CSTR) or even laminar flow pattern in tubular reactors, can accurately describe the real reactors. Nevertheless, this is not the case for many other situations, especially when higher volumes and/or more viscous mixtures are involved. Several important modifications in the ideal flow pattern can effectively occur, such as the formation of stagnant regions inside the real reactor, channeling and short-circuiting, internal recycle flows, and so on.

Residence Time Distribution (RTD) analysis is a very efficient diagnosis tool that can be used to inspect the malfunction of chemical reactors. It can also be very useful in modeling reactor behavior and in the estimation of effluent properties. This technique is, thus, also extremely important in teaching Reaction Engineering, in particular when the non-ideal reactors become the issue [3–9]. Laboratory classes are very important for students to interiorize and to validate experimentally theoretical concepts, allowing them to feel confident applying the RTD technique in a real situation. The development of didactic experiments, where students can attain the former objectives is a recursive task that must be continuously updated.

In this article we describe the approaches that have been used in the teaching of this subject in the Chemical Engineering courses in Instituto Superior Técnico (IST)—Universidade Técnica de Lisboa (UTL) and in Faculdade de Engenharia—Universidade do Porto (FEUP). Several experiments have been developed with the following main guide-lines:

- intrinsic safety;
- low price and low operation cost;
- environmental safety;
- high didactic content.

An integrated set of experiments has been used to allow the students to analyze working reactors (IST). The work involves determining RTDs, both by impulse and step tracer injection techniques, and applying them to the modeling of the reactor flow and to the estimation of the behavior of a nonlinear chemical transformation. Very simple forms of obtaining non-ideal reactor behavior are used, such as deficient agitation in continuous stirred tank reactors. The experiments are carried out in transparent reactors and using both colored tracers and a colored reaction, so that the student can readily see the evolution of tracer and reactant concentrations in the reactor during the transient behavior experiments.

The RTD technique has also been used for the experimental characterization of the flow pattern of a packed bed and a tubular reactor that exhibit, respectively, axially dispersed plug flow and laminar flow patterns (FEUP).

THEORY

Danckwerts [3] introduced the concept of 'fluid element', meaning a small volume of fluid where continuous properties, such as concentration, can still be defined. The RTD function, external residence time distribution, $E(t)$, measures the time that the various fractions of 'fluid element' reside in the reactor (macromixing); it gives no information about the mixing details at a molecular level (micromixing). The expressions of the RTD functions can be derived for the ideal reactors, as well as for any association of PFR and CSTR elements [4–6].

The $E(t)$ function of a real reactor can be obtained experimentally using stimulus-response techniques, by well-known methods of tracer injection. If an impulse of tracer is injected at the inlet, and its outlet concentration $C_T(t)$ is measured as a function of time, the experimental RTD function, $E(t)$, is obtained from the expression [4,6]

$$E(t) = \frac{C_T(t)}{\int_0^\infty C_T(t)\,dt} \tag{1}$$

The consistency of the results can then be tested: in the first place the total quantity of tracer injected, Ne, is compared to the total amount of tracer detected at the exit of the reactor

$$Ns = \int_0^\infty Q C_T(t)\,dt$$

where Q is the volumetric flow rate; and in the second place the effective mean residence time

$$\bar{t} = \int_0^\infty t E(t)\,dt$$

is compared to the expected value given by the ratio V/Q. Specific problems of by-pass and/or dead volumes formation within the real reactor can be detected by these tests.

A simple observation and comparison of the real RTD with the ideal reactor ones, allows a qualitative evaluation of the extent and, sometimes, of the nature of the pattern flow modifications. Further quantitative treatments in the pattern flow analysis can proceed through the modelization of the real reactor: an association of ideal reactors can then be proposed with a corresponding RTD that reasonably reproduces the experimental one.

The corresponding residence time distributions for the ideal flow patterns of PFR and perfect mixing in CSTR, and for the models of dispersed plug flow and laminar flow reactors, are [4]:

Ideal plug flow:

$$E(t) = \begin{vmatrix} 0 & \text{if } t \neq \bar{t}_r \\ \infty & \text{if } t = \bar{t}_r \end{vmatrix} \tag{2}$$

Perfect mixing reactor:

$$E(t) = \frac{e^{-t/\bar{t}_r}}{\bar{t}_r} \tag{3}$$

Axially dispersed plug flow reactor:

$$E(t) = \frac{\sqrt{\bar{t}_r\,Pe}}{2\sqrt{\pi t^3}} e^{-Pe(\bar{t}_r - t)^2/4\,\bar{t}_r \times t} \tag{4}$$

Laminar flow reactor:

$$E(t) = \frac{\bar{t}_r^2}{2t^3} H\left(t - \frac{\bar{t}_r}{2}\right) \tag{5}$$

where $\bar{t}_r$ is the average residence time, Pe is the Peclet dimensionless number, $H(t)$ is the Heaviside function and t is the time dimension.

Another important field of RTD applications lies in the prediction of the real reactor performance, since the known project equations for ideal reactors are no longer valid. Now the concepts of macro and micromixing are fundamental. For each macromixing level, expressed in the form of a specific RTD, there is a given micromixing level, which lies between two limiting cases, complete segregation and perfect micromixing. While in the first case a given 'fluid element' never contacts with 'fluid elements' possessing ages different than its own, in the second, all the 'fluid elements' meet all the others having a different age at the earliest possible stage.

In the case of complete segregation, each 'fluid element' can be considered as a small batch reactor, and the reactant concentration in it will be obtained directly from the kinetic law, as the element moves through the reactor. If $C_e(t)$ is the reactant concentration in a 'fluid element' with the residence time t, calculated from the mass balance of a batch reactor with the initial condition of $C_e(0) = C_i$ (reactant concentration at the entrance of the reactor), then the mean effluent concentration, $C(t)$, will be given by

$$C(t) = \int_0^t C_e(t)\,E(t)\,dt \tag{6}$$

where the sum of the contributions from the fluid elements is made between zero (those that exit as soon as they enter) and the instant t (those that have been in the reactor for t units of time), assuming that the reactant started to be fed at $t = 0$ [6]. The value of the reactant concentration in the steady-state, $C(\infty)$, will be obtained by extending this summation to all the range of residence times. This prediction of reactor performance is still correct in the case of non-segregated flow for first-order reactions. In fact, for the first-order processes the conversion depends only on the time spent in the reactor [7]. For other kinetic laws,

the reactant conversion will depend on its local concentration.

Zwietering developed a theoretical treatment for the prediction of outlet reactant concentration corresponding to the perfect micromixing case [8]. In addition to the exit-age distribution function, the 'life expectancy' function is used [4, 6]

$$\lambda(t) = \frac{E(t)}{\int\limits_t^\infty E(t)\,dt}$$

The final result is the equation

$$\frac{dC}{dt} = r(C) + \lambda(t)\left(C - C_i\right) \text{ with } \frac{dC}{dt}(\infty) = 0 \tag{7}$$

where $r(C)$ is the kinetic law, C_i the inlet reactant concentration, and t is the life expectation, *i.e.* the time the volume element will take to leave the reactor. The predicted outlet reactant concentration at the steady-state, according to the perfect micromixing approach, will be the value of C at $t = 0$ (reactor outlet zero life expectation).

The integration of this equation can be performed by the following procedure: the value of $C(\infty)$, at a large enough life expectation (for example, 6 mean residence time), is obtained from the condition $dC/dt(\infty) = 0$; starting at this reference, the desired value of $C(0)$ results from the backwards numerical integration.

This procedure has been exemplified, for instance, in reference [10].

EXPERIMENTAL ILLUSTRATIONS

We describe now four experiments that proved to be useful in helping students interiorize and validating the RTD technique concepts. These experiments cover the most important kind of
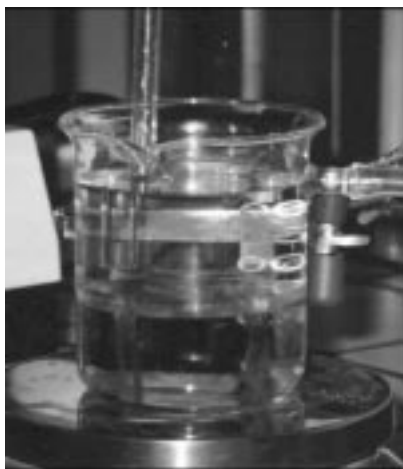

Fig. 1. Photo of the experimental apparatus of the real CSTR study.

tracer perturbations and reaction flow patterns. The *Stirred reactor with a stagnant volume* and *Two in series stirred reactors* experiments are taught at IST, while experiments *Packed bed reactor* and *Laminar flow tubular reactor* are taught at FEUP and are described in detail in reference [12]. All experiments are integrated in senior level classes, within the Chemical Engineering undergraduate curriculum.

Stirred reactor with a stagnant volume

In this work, a simple way of obtaining non-ideal reactor behavior is used, by combining a deficient agitation in a continuous stirred vessel with the presence of a division inside the vessel with two holes, in order to establish a weak communication between the two parts of the reactor (Fig. 1).

A solution of methylene blue is used as a tracer, which is injected in the reactor feed by impulse, or by step input. The tracer concentration at the exit of the reactor is evaluated by spectrophotometry, measuring the absorbance at 650 nm. The experimentally obtained RTD is used to allow the evaluation of the deviation of the real flow pattern from the perfect mixing. Several operating parameters are regularly changed, with important induced modifications in the obtained RTD: increasing the agitation speed results in an clear approximation of the real RTD to the ideal case; different positions of the inlet tube inside the reactor, as well as different flow rates, induce different flow patterns.

Figure 2 presents an example of the experimental data for the DTR, and the expected curve if the perfect mixing was effective,

$$E(t) = \frac{1}{\bar{t}_r} e^{-t/\bar{t}_r}$$

where $\bar{t}_r = V/Q$ is the expected mean residence time. The representation of a possible model that reasonably agrees with the experimental RTD is also presented; this model is a parallel association of two in-series ideal CSTR's batteries, constituted by 6 and 5 equal volume reactors, whose $E(t)$ function is

$$E(t) = \frac{Q_1}{Q} \frac{t^5}{5!\left(\frac{V_1}{Q_1 6}\right)^6} \exp\left(\frac{-tQ_1 6}{V_1}\right)$$

$$+ \frac{Q_2}{Q} \frac{t^4}{4!\left(\frac{V_2}{Q_2 5}\right)^5} \exp\left(\frac{-tQ_2 5}{V_2}\right) \tag{8}$$

where V_1 and V_2 are the volumes of the 6 and 5 tanks-in-series batteries, respectively, and Q_1 and Q_2 are the corresponding volumetric flows ($V_1 + V_2 = V$ and $Q_1 + Q_2 = Q$).

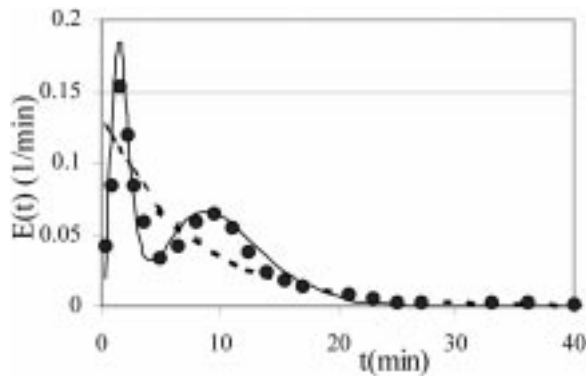The experiment considers the following main equipment, with approximate costs:

Fig. 2. Experimental DTR ($\bullet$), DTR for the ideal perfect mixing case (---) and model DTR (—).

- feed pump: €1250
- magnetic stirring device: €300
- spectrophotometer (Spectronick 20 D): €2200

Operating costs comprehend standard glass material and chemical products, and can be assumed marginal.

Two stirred reactors in series

The experimental apparatus of two in-series continuous stirred tanks is shown in Fig. 3. The reaction used in this work is the acid catalysed acetone iodination:

$$CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + HI.$$
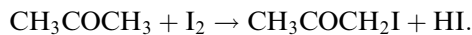
The rate law is [11]

$$r = \frac{C_H C_A C_I}{K_1 C_H + K_2 C_I}$$

where C_H, C_A, and C_I are the concentrations of the acid, acetone and iodine, respectively. The solutions of iodine, and of acetone, are pumped separately from the feed vessels. At the instant $t = 0$, these solutions are fed to the reactors, which are initially filled with solvent. The outlet reactant concentration is analysed by iodometry until the steady state is obtained. The values of k_1 and k_2 were obtained from a previous kinetic study. The results obtained for a given set of experimental conditions (Table 1) are presented in Fig. 4.

The experimental RTD of this system can be determined after the steady-state is obtained, maintaining all the experimental conditions, according to the procedure previously described

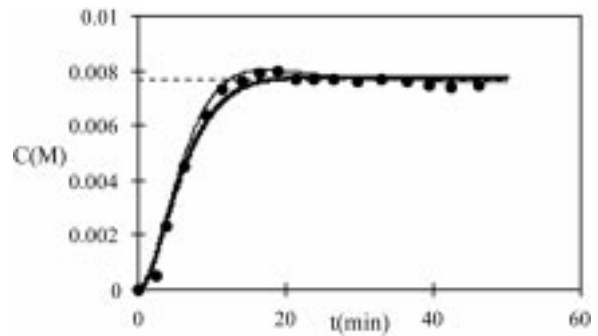Fig. 3. Photo of the two in-series CSTR apparatus.

Fig. 4. Iodine concentration as a function of time: experimental points ($\bullet$); complete segregation model (—); Zwietering equation for the steady state (---); mass balance (—).

for tracer impulse injection. In this case, the tracer used is an aqueous solution of $NiNO_3$; the tracer outlet concentration is measured by spectrophotometry, at 720 nm.

If the experiment is performed with enough stirring in the reactor vessels, the theoretical expression for $E(t)$ corresponding to a system of two in-series ideal CSTR reactors [6], with equal volume, $E(t) = t/\bar{t}_r^2 \exp(-(t/\bar{t}_r))$, can be successfully fitted to the experimental values of the RTD function; the adjusting parameter is $\bar{t}_r = 4.1$ min.

Considering the calculation of the total segregation approach, the rate expression has to be integrated by a numerical method, with the initial conditions presented in Table 1. From these integration results and taking the $E(t)$ function, the reactant concentration at the effluent of the reactor system for complete segregation is then computed. According to the procedure previously described, the iodine concentration prediction for the steady-state from the Zwietering equation is also obtained. The experimental results for the iodine concentration, as a function of time of reaction, as well as the predictions from the complete segregation and perfect micromixing approaches, are presented in Fig. 4. The results obtained from the integration of the mass balances for two in-series ideal CSTR's (assumes micromixing) are also included, since the experimental $E(t)$ values fitted very well to this model.

From the observation of this figure it is remarkable the close proximity between the reactor performance prediction from the theoretical approaches and the experimental values, especially for the steady-state. Since the acetone and acid concentrations inside a segregated fluid element are in excess relative to iodine concentration, the kinetics of the reaction can be reduced to apparent zero-order; if all the fluid element iodine concentrations lie in the range that satisfies the zero-order condition, $k_2 C_I \gg k_1 C_H$, which is approximately the case for this experience, the effect of micromixing in the conversion is not very relevant. Otherwise, if the reaction is performed at higher levels of conversion, so that a considerable number of segregated fluid elements does not satisfy the mentioned condition, the kinetics will be first order

Table 1. Experimental reaction conditions for the two in-series CSTR operation.

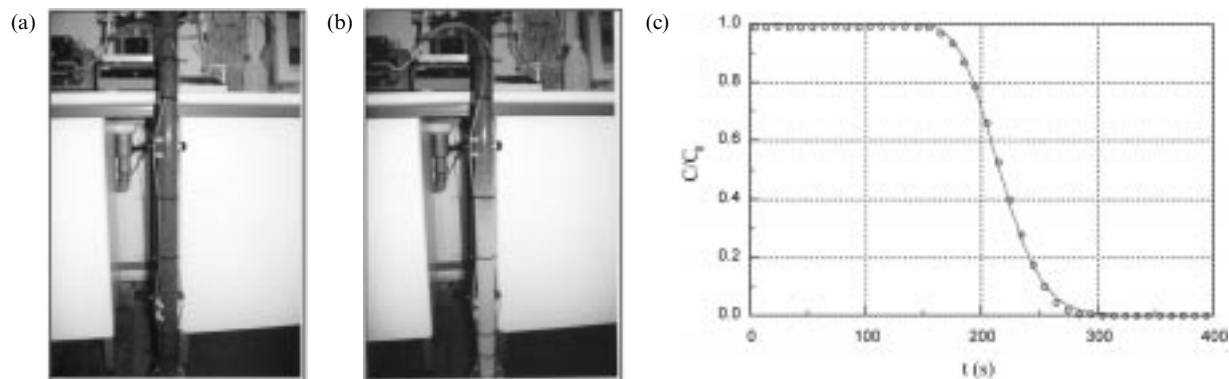| Entrance concentrations:	Reactor's volume $= 2 \times 245$ ml
$C_H = 0.17$ M; $C_A = 1.8$ M; $C_I = 0.012$ M	Flow rates: acetone $= 26$; iodine $= 33$ l/min
Rate constants: $k_1 = 0.05$; $k_2 = 640$ M min	T $= 19°$C

(a)   (b)   (c)

Fig. 5. Packed bed reactor, step purge experiment: a) start; b) approximately at the middle of the experiment; c) experimental results (points) and model fit (line).

in those lower iodine concentration elements, and the effect of micromixing between fluid elements where the effective kinetics is zero-order with those of first-order will be important in the conversion obtained; in this case the experimental results are much closer to the Zwietering prediction than to the segregation approach.

All the calculations can be easily carried out using commercial spreadsheet programs.

The experiment considers the following main equipment, with approximate costs:

- feed pump (2): €2500
- magnetic stirring device (2): €600
- spectrophotometer (Spectronick 20 D): €2200

Operating costs take into account standard glass material and chemical products, and can be assumed marginal.

Packed bed reactor

The packed bed reactor, shown in Fig. 5, consists of a 1.01 m long tube with an internal diameter of 0.036 m and containing glass beads of 0.003 m diameter.

The reactor is initially filled with a tracer solution of potassium chloride 0.1 M and 0.1% (w/w) carmine indigo (both species are environmentally safe and harmless for humans). A step purge is performed by feeding water at a known constant flow rate. The indigo indicator is present solely to add a visual element to the experiment, since the quantitative RTD determination is performed by measuring the conductivity of the KCl solution exiting the reactor. The condutimeter is connected to a computer through a RS-232 interface (the data acquisition rate is one point every two seconds). An example of experimental results can be seen in Fig. 5(c).

Students are asked to fit the axially dispersed plug flow reactor model to the measured data using the average residence time and Peclet number as fitting parameters. This can be easily done using, for instance, the 'solver' add-in available in MS Excel®.
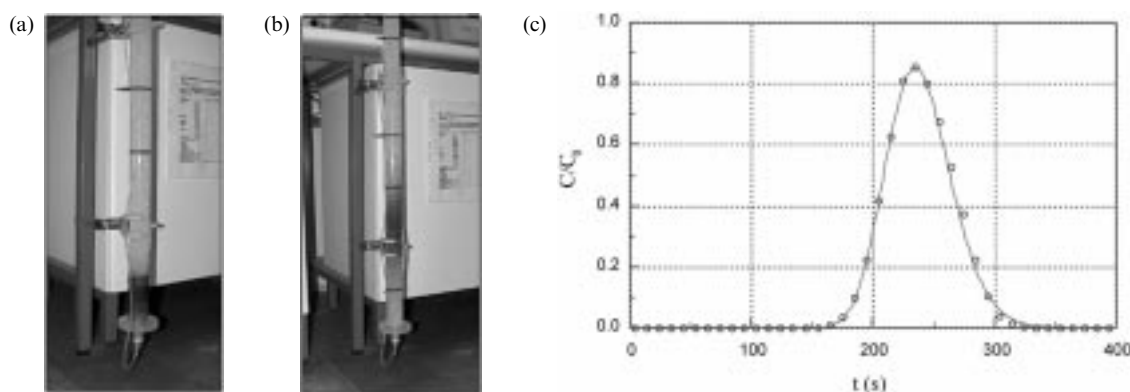
(a)   (b)   (c)

Fig. 6. Packed bed reactor, pulse perturbation experiment: a) initial stage; b) approximately at the middle of the experiment; c) experimental results (points) and model fit (line).

While a purge step can present some advantages over other forms of perturbation, a pulse perturbation is also widely used and students should also experiment with it. This can be done easily with the available experimental set-up, using an injection valve with a $20 \, cm^3$ loop. Figure 6 shows the pulse traveling across the reactor and the corresponding experimental result.

The experiment considers the following main equipment, with approximate costs:

- packed bed reactor: €150
- feed pump: €1000
- conductimeter and cell: €2000
- computer (does not include data acquisition software): €750
- injection valve: €450

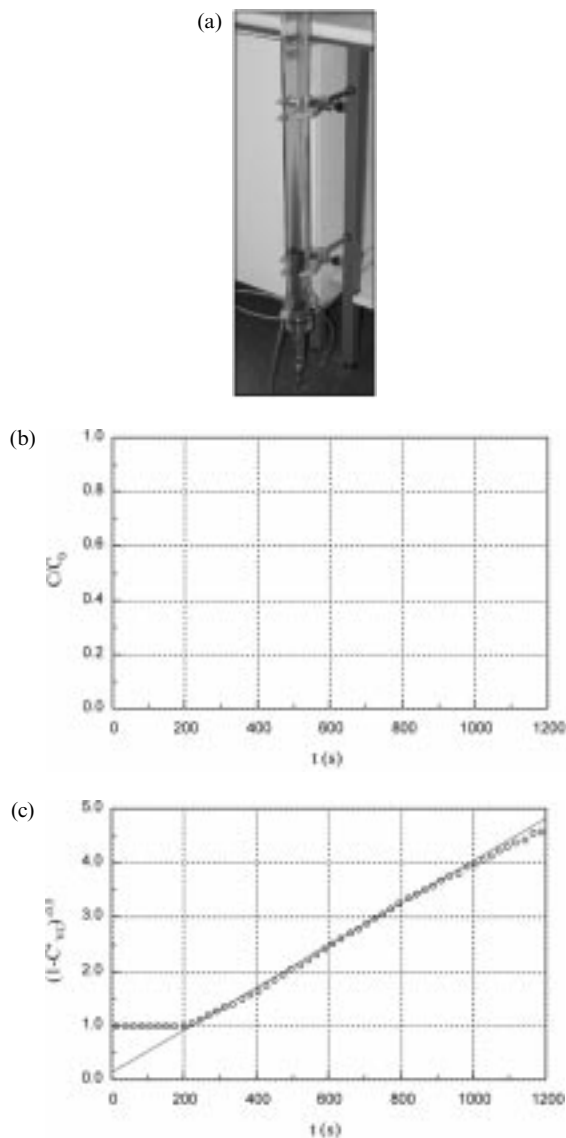Operating costs allow for the indicator solutions and can be assumed marginal.

Fig. 7. Tubular reactor, step perturbation experiment: a) a view of the tracer front traveling along the reactor; b) experimental results; c) experimental results (points) and linearized model fit (line).

Laminar flow tubular reactor

The tubular reactor is 1.01 m long and has an internal diameter of 0.022 m, see Fig. 7.

The reactor is initially filled with water. A step input in the inlet concentration is performed using a 5×10^{-6} M crystal violet solution. This kind of perturbation is the best for visualizing the characteristic parabolic shape of the concentration front, Fig. 7(a). The tracer concentration in the exiting stream is measured using a colorimeter, at a wavelength of 590 nm, and recorded into a computer.

This experiment demands special care, since convection streams, originated by density gradients associated to thermal and/or concentration differences inside the reactor, can easily disturb the laminar profile and ruin the results. Temperature must be kept constant and homogeneous throughout the reactor within $0.5°C$. To guarantee this thermal homogeneity, the reactor has an outside jacket connected to a refrigerated waterbath. The solutions fed to the reactor are kept in jacketed vessels also connected to the waterbath. All refrigeration and connecting tubes are thermally insulated.

In addition, the density of the tracer solution should be close to that of the liquid originally inside the reactor (water). Crystal violet is a very strong colorant that allows us to use very low concentrations. Also, the crystal violet solution should be made from the same water used to fill the reactor.

A conical diffuser at the reactor's entrance, filled with 1 mm diameter glass beads, minimizes turbulence that can be originated from the sudden inlet section change. A similar conical diffuser at the reactor's outlet allows for radial mixing of the exiting stream, approaching a plug flow pattern. Contrary to carmine indigo or potassium chloride, crystal violet (in the original powder form) is described by the manufacturer as being harmful, irritant and dangerous for the environment [13]. However, the extremely low concentration used, 5×10^{-6} M, minimizes these negative effects. This reactant is commonly used in microbiology at concentrations close to 2.5×10^{-3} M.

An example of experimental results is shown in Fig. 7(b). Figure 7(c) shows the linearization of the experimental curve and the model fitting line. It is clear from this figure how close to the ideal flow pattern this reactor behaves.

The experiment considers the following main equipment, with approximate costs:

- tubular reactor: €250
- feed pump: €1000
- colorimeter: €1000
- computer (does not include data acquisition software): €750
- thermostatic bath (heating and cooling): €2500

Operating costs allow for the indicator solutions and can be assumed marginal.

CONCLUSIONS

RTDs are an important concept in Chemical Reaction Engineering, usually lectured in mathematical detail, but lacking a practical perspective that is essential for the students' complete understanding. The experiments described here facilitate the interpretation of the phenomena involved by incorporating strong visual elements. Along the last years, student feedback, obtained from either formal or informal inquiries, has shown to be quite positive (global appreciation scores above 4 in 5).

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José Madeira Lopes is associate professor of chemical engineering at Instituto Superior Técnico, Technical University of Lisbon. He graduated in chemical engineering (1986) and earned his PhD in chemical engineering (1993) from Instituto Superior Técnico. His teaching areas are in the domain of chemical reaction engineering and process dynamics and control, and research interests in the domain of catalysis by zeolites.

Francisco Lemos is full professor of chemical engineering at Instituto Superior Técnico, Technical University of Lisbon. He graduated in chemical engineering (1981) and made his PhD in chemical engineering (catalytic processes) in 1989. He is currently teaching process dynamics and control and reactor dynamics at I.S.T. His research interests are in the area of catalysis and dynamical systems analysis and simulation.

Carla Pinheiro is assistant professor of chemical engineering at Instituto Superior Técnico, Technical University of Lisbon. He graduated in chemical engineering (1986) and earned his PhD in chemical engineering (1995) from Instituto Superior Técnico. His teaching areas are in the domain of chemical reaction engineering and process dynamics and control, and research interests in the domain of catalysis by zeolites and process dynamics and control.

Fernão Magalhães is assistant professor of chemical engineering at the Faculty of Engineering—University of Porto. He graduated in chemical engineering (1989) and earned his PhD in chemical engineering (1997) from the University of Massachusetts. He is teaching Chemical Engineering Laboratories and is working on the implementation of pilot-scale experiments, many industry-sponsored.

Adélio Mendes is associate professor of chemical engineering at the Faculty of Engineering—University of Porto. He graduated in chemical engineering (1987) and earned his PhD in chemical engineering (1993) from the same school. He is teaching Chemical Engineering

Laboratories, mainly chemical reaction engineering and non-conventional separation processes.

Carlos Costa is full professor of chemical engineering at the Faculty of Engineering—University of Porto. He graduated in chemical engineering (1972) and earned his PhD in chemical engineering (1984) from the same school. His research and teaching areas are in process systems engineering, design and complex systems and he is currently the dean of the Faculty of Engineering—University of Porto.

Fernando Ramôa Ribeiro is full professor of chemical engineering at Instituto Superior Técnico, Technical University of Lisbon. He graduated in chemical engineering (1968) from Faculdade de Engenharia da Universidade do Porto and made his Doctorat d'Etat (1980) at the Université de Poitiers (France). His teaching and research interests are in the areas of heterogeneous catalysis and catalytic reactors. He is a member of the American Institute of Chemical Engineers since 1991. He is currently President of National Foundation for Science and Technology.