

Predicting the Performance of a Chemical Reactor*

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This paper presents a laboratory illustration concerning the problem of chemical reactor performance prediction. Real-world reactor flow patterns rarely conform to the ideal cases of plug flow or perfect mixed flow, and the equations describing the latter will not be applicable. If it should be necessary to predict the performance of a reactor, without a complete physical description of the inner workings of the reactor itself, a different approach to that supplied by mass balances will be required. The experiment described in this paper involves the determination of the residence time distribution function of a given real reaction system, and the use of this information to predict the outlet reactant concentration. The limiting approaches of complete segregation and perfect micromixing are discussed and analysed. The results are compared to the corresponding experimental values of reactant concentrations, and the influence of the extent of micromixing is evaluated.

1. The paper describes new training tools or laboratory concepts/instrumentation/experimentation in:
Chemical reactor engineering. The laboratory experiment described is used to illustrate concepts used in chemical reactor engineering, namely in respect to residence time distribution functions and extent of micromixing and their relation to chemical reactions.
2. The paper describes new equipment useful in the following courses:
The paper does not describe any new equipment.
3. Level of students involved in the use of the equipment:
The experiment described does not make use of very specialized equipment, but the concepts that are used are useful for chemical engineering students in their higher years, probably associated with chemical reaction engineering laboratories and the study of transient state reactors.
4. What aspects of your contribution are new?
The approach that is made to the problem and the kind of illustration that can be given using the whole of the experiment. The use of commercial programmes in IBM-compatible computers to solve the mathematics of the various approaches, including Zwietering's equation for complete micromixing.
5. How is the material presented to be incorporated in engineering teaching?
This material is best used in association with a course on reactor dynamics and real reactors. It can illustrate the problems of non-linear kinetic rate laws and the performance and transient state of reactors.
6. Which texts or other documentation accompany the presented materials?
As far as laboratory sessions are concerned, a laboratory guide for the experiments and questionnaires concerning the experimental execution are supplied. The whole course is supported by a chemical reactor analysis and design book (usually Froment and Bischoff [8]).
7. Have the concepts presented been tested in the classroom? What conclusions have been drawn from the experience?
The work presented has been used for at least 4 years in the laboratory of a course on reactor dynamics, for the last year of a chemical engineering degree with good results.

INTRODUCTION

THE MACROSCOPIC flow pattern in a continuous reactor lies normally between two limiting cases, the well-known idealized plug flow (PFR) and perfect mixed flow (CSTR) approaches. The problems associated with scale-up are frequently related to the non-ideality of flow, which can

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represent a loss of conversion when comparing the performance of a small unit with that of a large one.

The residence time distribution (RTD) functions provide information about the flow pattern at a macroscopic level, describing how long individual fluid elements stay in the reactor. The expressions of these functions can be derived for the ideal cases mentioned above, as well as for any association of PFR and CSTR elements [1–3]. Each real flow pattern through a vessel is associated with a specific RTD function, whose values can be obtained experimentally using the stimulus–response technique. Nevertheless, a number of flow patterns can give the same RTD, depending on the extent of micromixing.

The important concept of ‘fluid element’ was introduced by Danckwerts [4], meaning a small volume of fluid, relative to the vessel dimensions, but large enough so that continuous properties, such as concentration, can be defined. The RTD function measures the time that these various fractions of fluid reside in the reactor (macro-mixing), but gives no information about the mixing details at a molecular level (micromixing). So, for a given macromixing pattern (e.g. RTD), a number of different can exist between complete segregation and perfect micromixing, depending on the extent of micromixing.

For a given reaction system, the particular RTD associated with the flow in the reactor vessel will significantly affect its performance. If complete segregated flow is effective, it is possible to predict exactly and easily the conversion in a real reactor, at any instant, from the RTD function. In the case of other micromixing states, this prediction is still valid for some reaction systems, the deviation being dependent of the reaction kinetics. The performance of the reactor can also be predicted for the perfect micromixing cases, at the steady-state, through the Zwietering equation, although not so easily.

The study of the dynamic behaviour of a continuous reaction system is obviously important. It is absolutely necessary in the case where an efficient control system has to be designed. The mass balances corresponding to ideal flows do not predict the performance of a real reactor with a different flow pattern, especially in large reacting units and/or when processing viscous mixtures.

A simple stimulus–response experiment can be easily performed at any reactor system, leading to the determination of the RTD function, and subsequently to the possibility of predicting the reactor behaviour, whatever the flow pattern.

In this article we present a practical example, suitable for laboratory illustration and mathematical treatment, concerning the problem of the predictability of reactor performance. For this purpose we chose a reaction with a non-linear kinetic rate equation, as we will see below.

The use of computers is strongly encouraged for the mathematical treatment associated with these processes. In particular, the development of curve-

fitting and numerical integration applications using spreadsheets enable a relatively easy experimental data treatment and theoretical predictions, as well as the construction of simulation models that are, apart from other fields of application, of great interest for didactical purposes [5, 6].

The main objectives are as follows:

- Experimental RTD determination of a reaction system and its use for reactor performance prediction through complete segregation and perfect micromixing approaches.
- Comparison between the predictions and the experimental reactant conversion.
- Evaluation of the micromixing effect on reactor performance.

THEORY

We will be interested in the application of RTDs to the prediction of reactor performance. The exit age-distribution function, $E(t)$, is a probability density function defined as $E(t)dt =$ fraction of volume elements at the outlet with a residence time between t and $t + dt$.

The experimental values for the $E(t)$ function can be obtained through the well-known method of tracer injection: the tracer is injected at the inlet and its outlet concentration $C_T(t)$ is measured as a function of time [1, 3]. If the tracer is injected as a pulse at $t = 0$, from such an experiment, and considering the definition of $E(t)$, we can calculate the experimental RTD by the expression:

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

Since $E(t)$ is not sensitive to all parameters related to the flow pattern in a reactor, it is possible to have several different reactors possessing the same RTD and having different performances.

To illustrate better the differences between the two limiting cases—complete segregation and perfect micromixing—they can be visualized by the two models presented in Fig. 1.

In both models the general reactor is associated with a plug flow reactor. In (a) all the reactant is fed to the reactor in the same spot but it is removed along the axis so that $E(t)$ is met, while in (b) the reactant is fed along the axis of the reactor so that the suitable $E(t)$ function is obtained. While in the first case a ‘fluid element’ never contacts with ‘fluid elements’ of different ages to its own, in the second all the ‘fluid elements’ meet all the others of 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. So, the conver-

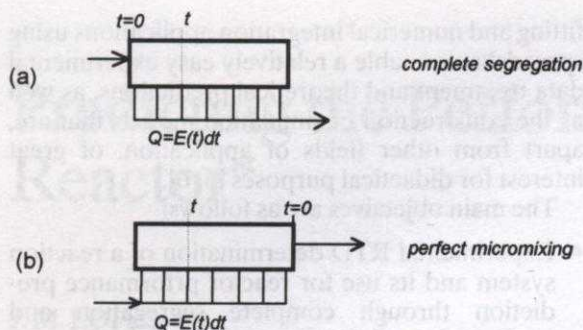


Fig. 1. Complete segregation and perfect micromixing modeling by a plug-flow reactor.

sion obtained at the exit of the reactor in each element depends solely on its residence time.

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:

$$C(t) = \int_0^t C_e(t)E(t)dt \quad (2)$$

where the sum of the contribution from the fluid elements is made between zero (fluid elements that exit as soon as they enter) and the instant t (fluid elements that have been in the reactor for t units of time), assuming that the reactant started to be fed at $t = 0$. The value of the reactant concentration for the steady-state, $C(\infty)$, will be obtained by extending this summation throughout the range of residence times. This is formally the global mass balance to model (a) [2].

The prediction of reactor performance through Eq. (2) is still correct in the case of non-segregated flow for the zero and first-order reactions. In fact, for zero-order processes, the reactant consumption is independent of its concentration, and 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, and Eq. (2) does not predict the exact effluent concentration for non-segregated flow, since the RTD is not a complete description of the flow pattern. The extent of micromixing will determine how molecules of different ages encounter one another in the reactor, and may also constitute an important parameter of reactor performance. Meanwhile, the effect of micromixing on the reactor performance is generally smaller than the effect of the RTD function.

Zwietering developed a theoretical treatment for the prediction of outlet reactant concentration corresponding to the perfect micromixing case based on the mass balance to model (b) (Fig. 1) [8]. In addition to the exist-age distribution function, the 'life expectancy' function is used:

$$\lambda(t) = \frac{E(t)}{\int_0^{\infty} E(t)dt}$$

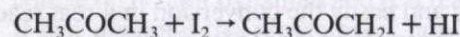
The final result is Eq. (3):

$$\frac{dC}{dt} = r(C) + \lambda(t)(C - C_i) \text{ with } \frac{dC}{dt}(\infty) = 0 \quad (3)$$

where $r(C)$ is the kinetic law, C_i the inlet reactant concentration, and t the life expectation, i.e. the time the volume element takes to leave the reactor. The predicted outlet reactant concentration at the steady state, according to the perfect micromixing approach, will be given by the value of C at $t = 0$ (reactor outlet corresponds to zero life expectation). The integration of Eq. (3) can be performed by the following procedure: the value of $C(\infty)$, at a large enough life expectation (e.g. $\sim 6 \times$ mean residence time), is obtained from the condition $dC/dt(\infty) = 0$; starting at this reference, the desired value of $C(0)$ results from backwards numerical integration.

EXPERIMENTAL APPARATUS AND PROCEDURE

The reaction performed in this work is acid-catalysed acetone iodination, according to the following stoichiometric equation:



The obtaining rate law, which is beyond the scope of this work, can be done by the application of the steady-state treatment to the reaction mechanism [9]:

$$r = \frac{C_H C_A C_I}{K_1 C_H + K_2 C_I} \quad (4)$$

where C_H , C_A , and C_I are the concentrations of the acid, acetone, and iodine, respectively, and K_1 and K_2 are global rate constants.

A schematic representation of the experimental apparatus is shown in Fig. 2.

The reaction system is composed of two continuously stirred reactors of equal volume. It is important to be aware that the reactor vessels must be closed and that the reaction effluent must be collected in another closed vessel, to prevent the irritation of the eyes caused by the iodinated acetone. The aqueous solutions of iodine (containing $\sim 1\%$ KI and the acid catalyst), and of acetone are pumped separately from the feed vessels, and their volumetric flow rates measured by positioning correctly the three-way valves. After that, at the instant $t = 0$, these solutions are fed to the reactors, which are initially filled with solvent (water).

Periodically, samples of the reactor effluent are taken and neutralized with sodium acetate 1 M to stop the reaction; the samples are analysed by

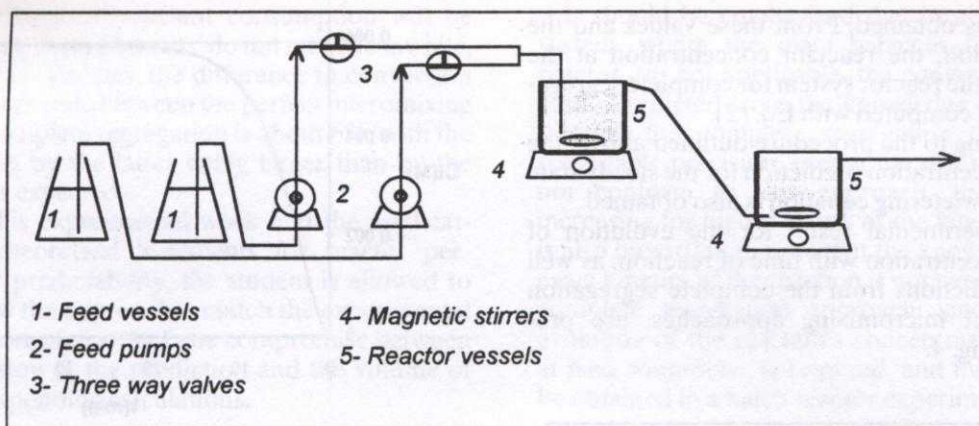


Fig. 2. Schematic diagram of the reaction apparatus.

iodometry, by titrating the iodine with sodium thiosulphate. The usual precautions concerning iodometric titrations must be taken [10]. The evolution of the outlet reactant concentration is thus analysed from the beginning of the feed until the steady state is obtained. The experimental conditions are listed in Table 1. The values of K_1 and K_2 were obtained at 19°C, from a previous kinetic study.

The experimental values for the $E(t)$ function are determined after the steady-state is obtained, maintaining all the experimental conditions. The tracer used is an aqueous solution of NiNO_3 (~1 g/ml); 10 ml of tracer are injected at the entrance of the first reactor and the tracer outlet concentration is analysed and registered as a function of the residence time, by spectrophotometry, at 720 nm. The measured absorbances, $A(t)$, proportional to the concentrations, allow us to calculate the $E(t)$ values through the expression

$$E(t) = A(t) / \int_0^{\infty} A(t) dt$$

RESULTS

$E(t)$

The theoretical expression for $E(t)$ corresponding to a system of two in-series CSTR reactors with equal volume [3]:

$$E(t) = \frac{t}{\theta^2} \exp\left(-\frac{t}{\theta}\right) \quad (5)$$

was fitted to the experimental values of the exit-age distribution function. The fitted curve and the experimental points are represented in Fig. 3, and show a very good fitting, the adjusting parameters being $\theta = 4.09$ min.

Reactant concentration

Euler's method was used to integrate the rate expression, Eq. (4), with the initial conditions presented in Table 1. The iodine concentration at each 'fluid element' as a function of its residence

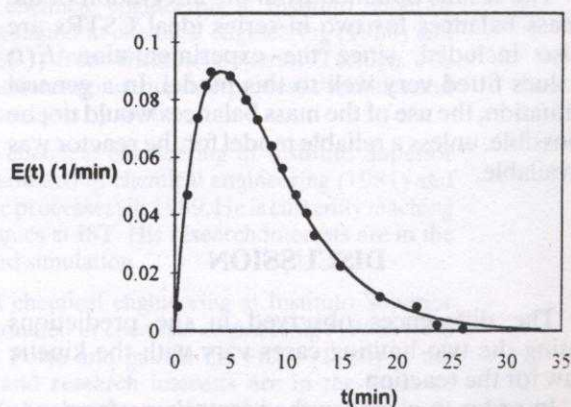


Fig. 3. Exit-age distribution function, $E(t)$, for the reaction system and operating conditions presented before; fitted curve Eq. (5) and experimental values.

Table 1. Experimental reaction conditions

entrance concentrations: $C_H = 0.168 \text{ M}$ $C_A = 1.84 \text{ M}$ $C_I = 0.0117 \text{ M}$	reactor's volume = $2 \times 245 \text{ ml}$ flow rates: acetone = 26 ml/min iodine = 33 ml/min
rate constants: $K_1 = 0.05 \text{ Mmin}$ $K_2 = 640 \text{ Mmin}$	$T = 19^\circ\text{C}$

time is thus obtained. From these values and the $E(t)$ function, the reactant concentration at the effluent of the reactor system for complete segregation is then computed with Eq. (2).

According to the procedure outlined above, the iodine concentration prediction for the steady state from the Zwietering equation is also obtained.

The experimental result for the evolution of iodine concentration with time of reaction, as well as the predictions from the complete segregation and perfect micromixing approaches, are presented in Fig. 4.

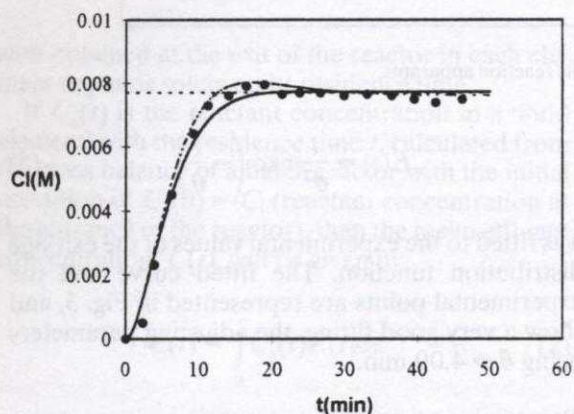


Fig. 4. Iodine outlet experimental concentrations as a function of the reaction time (\bullet) and prediction through complete segregation (—), perfect micromixing approaches (---) and from the mass balances (— · —).

The results obtained from the integration of the mass balances for two in-series ideal CSTRs are also included, since the experimentation $E(t)$ values fitted very well to this model. In a general situation, the use of the mass balances would not be possible, unless a reliable model for the reactor was available.

DISCUSSION

The differences observed in the predictions using the two limiting cases vary with the kinetic law for the reaction.

In order to compare the reactor's performance predictions for other kinetic rates and to illustrate better the point presented above, the complete segregation and perfect micromixing calculations were also performed considering a first-order kinetic law (Fig. 5) and a third-order kinetic law (Fig. 6), relative to iodine concentration, under identical operating conditions. The rate constants were adjusted so that the resulting conversions were similar: $K_1 = 0.1 \text{ min}^{-1}$, $K_2 = 2500 \text{ M}^{-2} \text{ min}^{-1}$.

Figure 4 shows the remarkably close proximity between the reactor performance prediction from the theoretical approaches and the experimental values, especially for the steady-state. For the transient response there is a slight difference

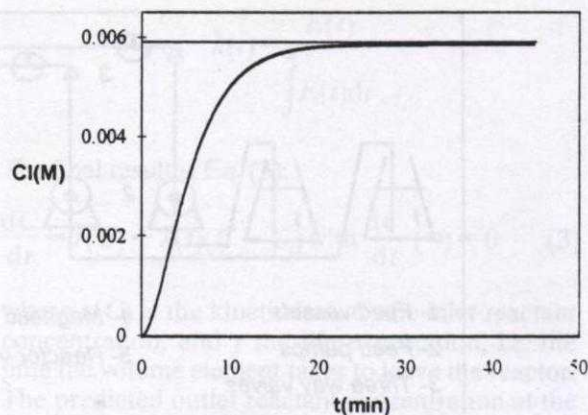


Fig. 5. Iodine concentration from complete segregation (—), perfect micromixing (---) approaches and from mass balances (— · —) (coincident with complete segregation) for first-order kinetics.

between the complete segregation and the mass balance integration results.

Although the difference in steady-state concentration between the methods presented is quite small, it is clear that the experimental results are closer to the mass balances transient curve than to the complete segregation prediction. In fact, it would be expected that a reaction system with a non-viscous liquid would deviate significantly from complete segregation. It is also important to note that the perfect micromixing approach probably over-emphasizes micromixing. In the present case we know that our reactor is composed of two separated vessels with no mixing between them. This is not taken into account at all in solving the Zwietering equation, which would then give a higher extent of micromixing than in the real reactor.

For the hypothetical case of first-order kinetics, the agreement between the predictions is even better, as expected. Considering a third-order kinetics case, it is now evident that there are some differences between all the limiting approaches. The lower reactant concentration obtained for the complete segregation is understandable consider-

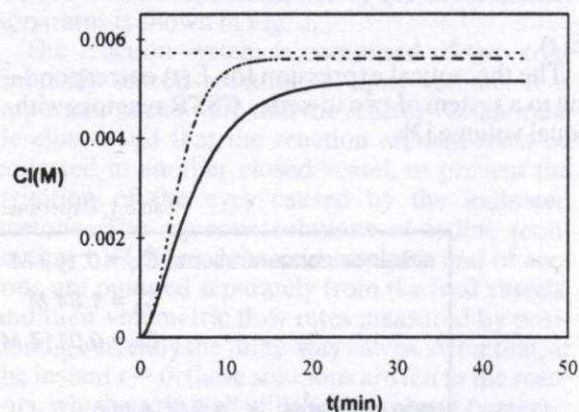


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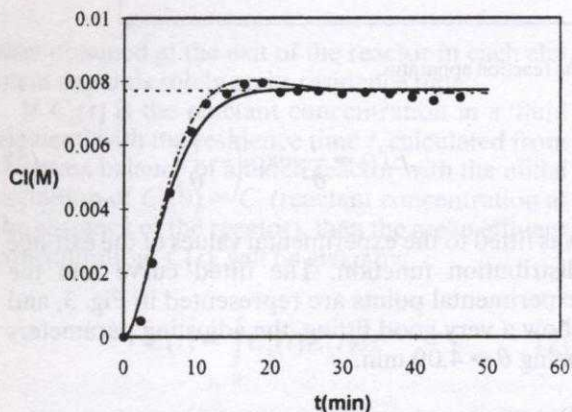


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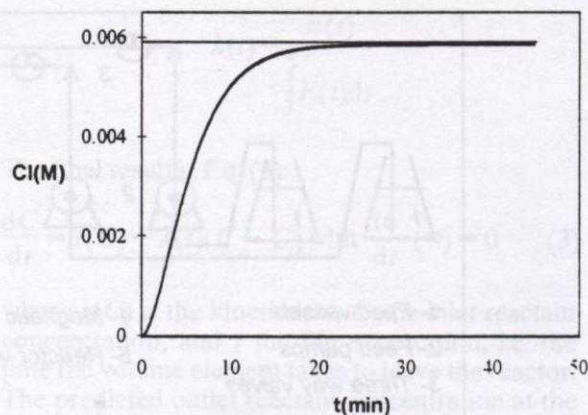


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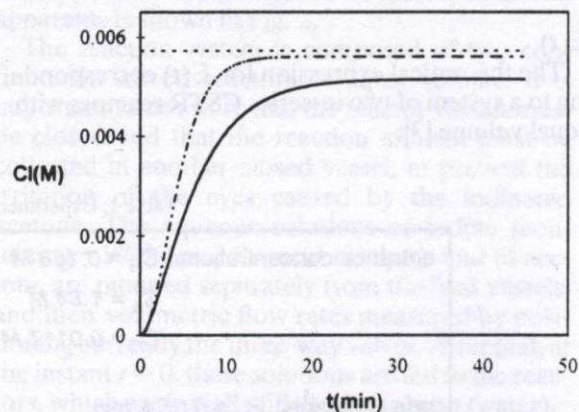


Fig. 6. Iodine concentration from complete segregation (—) and perfect micromixing (---) approaches and from mass balances (— · —) for third-order kinetics.

ing that the local reactant consumption will be higher if the 'fluid elements' do not mix. Meanwhile, even for this kinetics, the difference in conversion at the steady state between the perfect micromixing and the complete segregation is about 6%, with the conversion by the latter being larger than by the former, as expected.

With this experimental work and the applications of theoretical treatments for reactor performance predictability, the student is allowed to verify how the approaches match the experimental observation, and to 'feel' the compromise between the precision of the prediction and the volume of the corresponding calculations.

It should be emphasized that in a real reactor system, where the mass balances for an ideal reactor are not applicable, the conversion can be easily predicted from the knowledge of the RTD through the complete segregation case with a reasonable precision, even if the real reactor does not conform to this approach, the deviation increasing for higher values of the kinetic order. It is also important to note that the knowledge of the exact kinetics of the reaction is not necessary in the complete segregation approach, since only the evolution of the reactant's concentration, starting at feed conditions, is required, and this can easily be obtained in a batch reactor experiment [1].

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