# Residence Time Distribution for Tubular Reactors

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**Abstract:** In the core of Chemical Engineering is the reactor design that includes most of all scientific disciplines. The reactor, in general, are treated ideally: mixed and plug-flow patterns. Unfortunately, it is observed in the real world a very different behavior from that expected. Thus, to characterize nonideal reactors is used, among others, residence time distribution function E(t), mean residence time $t_m$ and cumulative distribution function F(t). The aim of this present work is to determine in the Comsol Multiphysics a distribution of residence time of a tubular reactor that is used, didactically, in the Chemical Engineering Laboratory in Federal University of Parana. The results were compared with experimental dates that concluded the modeling of the reactor showed good agreement according to the correlation coefficient of 0.97. At last, it was purposed a modification in the reactor's geometry to take note with its hydrodynamic would get better.

**Keywords:** Residence Time Distribution (RTD), Simulation, COMSOL Multiphysics, Nonideal Reactors.

## 1. Introduction

The Chemical Reaction Engineering (CRE) that includes in its scope the design of reactors uses information, knowledge and experience from areas such as thermodynamics, mass transfer, chemical kinetic, fluid mechanics, heat transfer and economic analysis. In general, the modeling processes involved in CRE establishes idealized systems, with assumptions of perfect mixing in the CSTR (Continuous Stirred Tank Reactor), slug flow in PFR (Plug Flow Reactor) and uniform composition in the case of Batch Reactors. However, in spite of the simplified mathematical treatment, many of cited assumptions lead to real reactor behavior itself far from ideal, mainly with the capacity and products distribution with significant deviations that may be caused by preferential flow path formation, recirculation and dead zone [1, 2].

It is nature to conclude how important is to consider no-idealities in the reactor design process.

Overall three interrelated factors make up the contacting or flow pattern to account deviations from idealities mentioned [2]:

1. The RTD or residence time distribution of material which is flowing through the vessel.
2. The state of aggregation of the flowing material, its tendency to clump and for a group of molecules to move about together.
3. The earliness and lateness of mixing of material in the vessel.

Light was placed just in the first statement. Thus, the residence-time distribution (RTD) is a characteristic of the mixing that occurs inside the chemical reactor [1].

Deviation from ideal flow patterns can be caused by channeling of fluid, by recycling of fluid, or by creation of stagnant regions in the vessel [2].

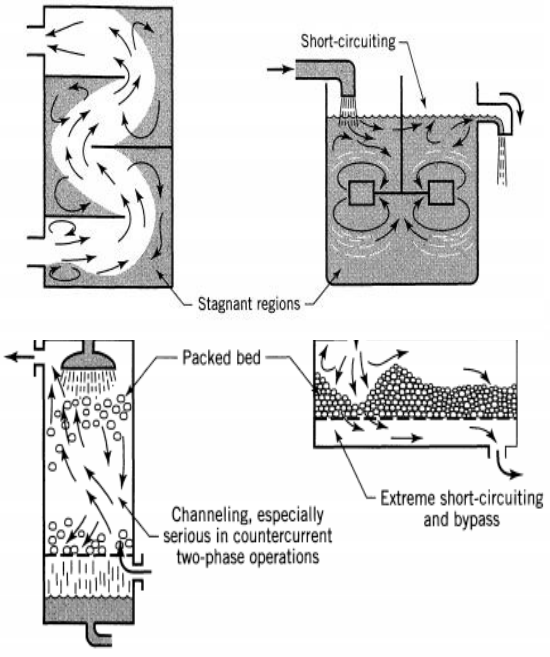


**Figure 1** - Nonideal flow patterns [2].

In all types of process equipments, such as heat exchangers, packed columns, and reactors, the type of flow showed, Figure 1, should be avoided since they can lower the performance of the unit [2].

### 1.1 Measurement of the RTD

The RTD is determined experimentally by injecting an inert specie, called tracer, into the reactor at some time and then measuring the tracer concentration, C, in the effluent stream over time [1,2,3]. The tracer must be a nonreactive specie, easily detectable and should have physical properties close to the reacting mixture, in other words, it should be soluble in the system. In addition, among others, the tracer's behavior must reflect the material flowing through the reactor.

There are, mainly, two used methods of tracer's injection called pulse input and step input [1].

In a pulse input, tracer is, suddenly, injected in one shot into the feed stream, entering the reactor in as short a time as possible. Since the step input consider a constant rate of tracer addition from an initial time, t = 0 t.u., before it, there is no tracer been added to the feed. The outlet concentration is measured over time, in both methods showed [1,2,3].

In order to become more understandable what was brought, there is a scheme below, Figure 2.

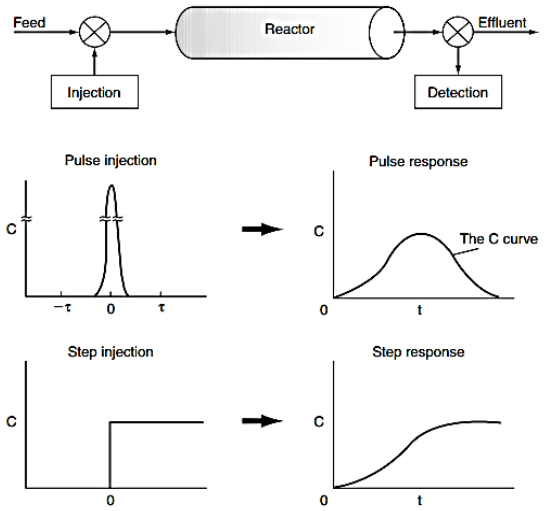


**Figure 2** - RTD measurements [1]

Focusing on the test method step (injection of tracer), illustrated in Figure 2, it can be seen that at beginning the concentration of tracer is low, however increases with time due to the flux in the reactor.

At first, the concentration of tracer is low, however increases with time due to the flux in the reactor. The fact that the response step is not equally the same is due to occurrence of dispersions in the system, which affects the mean residence time in the reactor and consequently, alters its conversion, yield and capability.

If $C_o$ is the concentration of tracer added to the reactor inlet, the F fraction of the tracer at the outlet of the reactor will be:

$$F(t) = \frac{C(t)}{C_o} \qquad (1)$$

The tracer concentration in the reactor outlet is given by:

$$C(t) = C_0 \int_0^t E(t)dt \qquad (2)$$

Substituting (2) into (1), it follows that:

$$F(t) = \int_0^t E(t)dt \qquad (3)$$

$$E(t) = \frac{dF(t)}{dt} \qquad (4)$$

Thus, the curve of distribution of residence time is obtained, Figure 3.

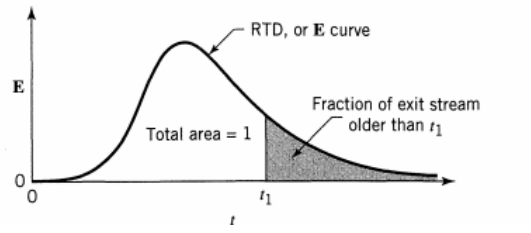


**Figure 3** - RTD curve behavior [2]

After obtaining the curves of concentration (curve C), the fraction of material in the reactor outlet (curve F), and the residence time distribution (curve E), all of them can be analyzed qualitatively and the behavior of the flow inside the reactor can be observed.

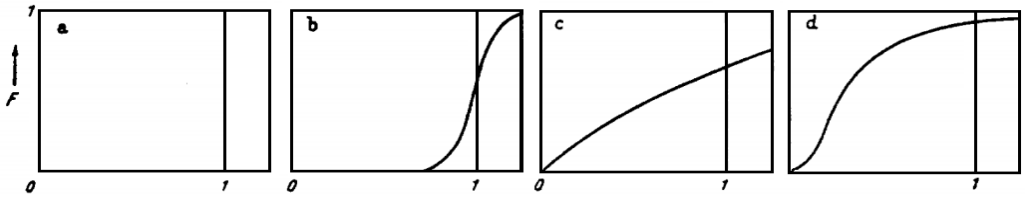


**Figure 4** - F-diagrams: (a) piston flow; (b) piston flow with some longitudinal mixing; (c) complete mixing; (d) dead water [4]

For example, the curve F can assume four different aspects according to the flow tracer, as Figure 4 shows.

Another important parameter to determine is the residence time, τ. Conceptually, it is the time that certain amount of molecules have remained within a unit volume. For a flow rate Q into a fixed volume reactor V, it is known that the mean residence time ideal is given by:

$$\tau = \frac{V}{Q} \qquad (5)$$

Strictly, the mean residence time for a real flow is given by the following expression:

$$\bar{t} = \int_0^\infty tE(t)dt \qquad (6)$$

The closer are the results of equations (5) and (6), closer the system will be of the ideality.

## 2. RTD experimental data acquisition

To make the acquisition of experimental data and compare with the data from COMSOL Multiphysics simulation, it was used a similar system to the Figure 3. Thus, the reactor, completely filled with NaCl (Brine), started to receive water, step test. Over time, the solution's concentration was measured, with a conductivimeter, in the reactor outlet. The results can be viewed in item 4.

## 3. Use of COMSOL Multiphysics

In order to obtain the behavior of the flow in the reactor inlet due to the difference in diameters of its inlet nozzle and its body, it was selected a 3D modeling. The used physics were laminar flow – since the flow used in the experiment was low - and transport of diluted species in view of brine's concentration used as tracer.

The model's geometry was constructed to represent the real equipment. Furthermore, cut up the geometry in half with a plane of symmetry, in order to better visualize the flow lines, the dispersion of the tracer as well as reduce the computational effort.

In relation to the properties of the material used, it approached the density and dynamic viscosity of the fluid flowable - brine - for pure water at the temperature at which the experiment was conducted by interpolation physic-chemical data Tables [5].

Diffusivities, at 25 ° C, o the chemical species involved ($Na^+$ and $Cl^-$) were taken from the literature [6] and corrected by the experiment temperature, according to the following expression [7]:

$$\frac{D_T}{D_{25\,°C}} = \frac{\mu_{25\,°C}}{\mu_T} \qquad (7)$$

### 3.1. Reactor modeling

#### 3.1.1 Laminar Flow

The equation that models the flow of fluid throughout the reactor is the Navier-Stokes equations.

$$\rho(u.\nabla)u = \nabla.[-pI + \mu(\nabla u + (\nabla u)^T] + F \qquad (8)$$

Where, u is the velocity vector, ρ is the density of the fluid, μ is the viscosity, p is the pressure and F is a body force term, such as gravity.

As the flow is incompressible,

$$\rho\nabla.u = 0 \qquad (9)$$

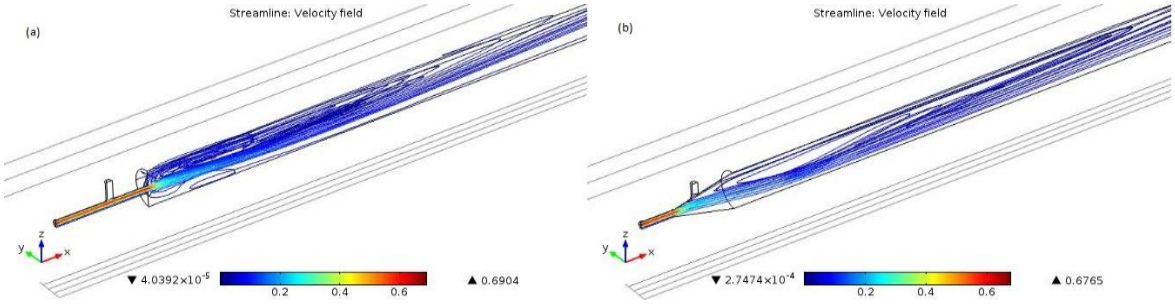


**Figure 5** – (a) Original Reactor; (b) Modified Reactor

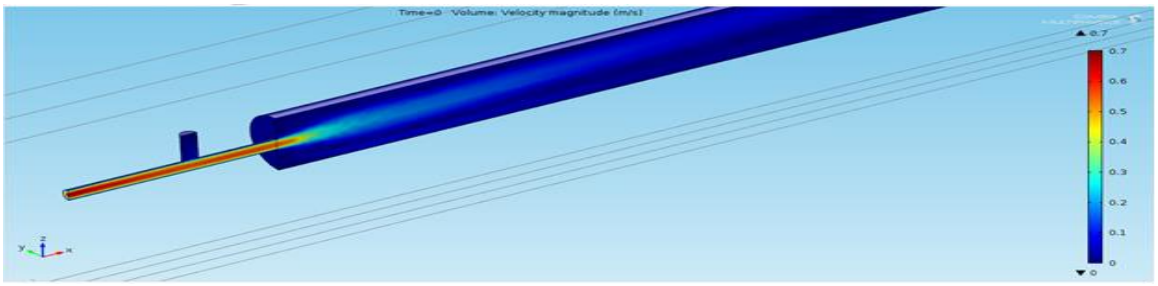

**Figure 6** - Tracer injection

The boundary conditions used to solve the equation were the input, output and speed in the reactor wall. Thus, it was used in the input condition the flow rate that is equal to the output, since the flow is stationary. In addition, the output condition has been chosen as the discharge pressure of the reactor, in this case, the atmospheric pressure. Finally, it was selected the condition of no slip on the walls of the reactor (zero speed).

The mesh size element was calibrated for fluid dynamics, and left to "normal" size - the highest possible for that particular calibration.

The direct method was employed for the solver as suggested for problems involving the resolution of the Navier-Stokes equation [8].

### 3.1.2 Transport of Diluted Species

The phenomena of tracer's diffusion and convection, Figure 6, are modeled by the continuity equation together with the equation of the overall flow:

$$\frac{\partial c_i}{\partial t} + \nabla.(-D_i \nabla c_i) + u.\nabla c_i = R_i \qquad (8)$$

$$N_i = -D_i \nabla c_i + u c_i \qquad (9)$$

Where, $c_i$ is the tracer's concentration, $D_i$ is diffusivity and $N_i$ is the diffusion flux.

Thus, to simulate the mass transport of the tracer inside the reactor was selected as boundary conditions the input, output and initial concentration values. The velocity field used was imported from the laminar flow study, described above. The concentration of the input was chosen to be zero (since water from the city supply was injected into the reactor, free of brine), while the initial value of concentration inside the machine was 445 mol/m³ (first measured in the reactor outlet).

The concentration provided by the model is a measured defined in the outlet contour.

### 3.2 Proposed modification of the Reactor

In order to reduce the non-idealities of flow, evaluated a modification of the inlet nozzle of the reactor geometry, as shown in Figure 5b, to monitor the expansion of the flow lines.

## 4. Results and Discussion

To validate the model used in the simulation was compared concentration data obtained experimentally with those provided by the

software, the correlation coefficient equal to 0.97.

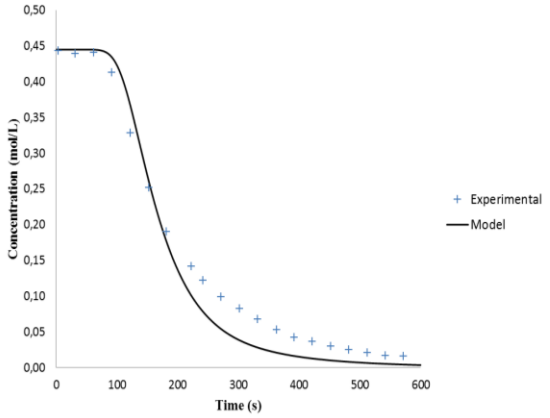


**Figure 7** - Reactor outlet concentration

From equations (1) and (4) it is possible to obtain the residence time distribution, Figure 8.

Furthermore, it was calculated the residence time average for the model and for the experiment.

The values obtained was 3.05 and 3.38 min, respectively. A deviation of 9.8%.

With the validated model, was verified with the simulation, the hydrodynamic behavior of the flow - preferred paths, areas of recirculation and stagnant zones - allowing for the non-ideality of the reactor. In Figure 5, the flux lines of the original and modified reactors are represented.

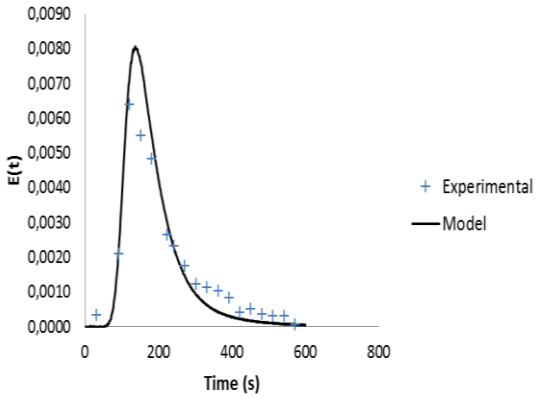


**Figure 8** - RTD curve

It can be seen that the implemented modification generates less recirculating fluid, indicating that the flow is more homogeneous; consequently, preferred ways are not favored. So, there is an increase in the residence time that can be verified through the curves E, Figure 9.

To compare with the value of the mean residence time, space-time was calculated, $\tau$, ideal flow, which is 6.10 min.

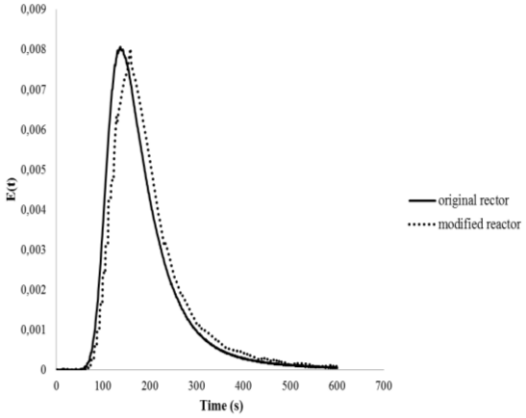


**Figure 9** - RTD curve of original and modified reactor

Thus, it can be established that as the space-time is twice greater than the mean residence time, there is a strong trend that is occurring preferential flow paths. Furthermore, by modifying the reactor there is an increase in the RTD, which leads to a decrease in e recirculation zones, Figure 6, favoring a more homogeneous flow.

## 5. Conclusions

According to the results, it is observed that the modeling of the reactor showed good agreement with the experimental results, the correlation coefficient of 0.97. Furthermore, with simulation it was possible to verify the hydrodynamic behavior of the flow - preferred paths, areas of recirculation and stagnant zones - allowing to establish the non-ideality of the reactor. The studies showed a space-time of 6.10 min. and an average residence time of 3.05 min (original reactor) and 3.38 min (modified reactor). Importantly that closer are values of space-time and residence time average, there is an indication that the reactor will operate more adequately. However, the hydrodynamic problems are not obvious, that is why the importance of computational fluid dynamics in the analysis, design and operation of reactors.

## 6. References


1. Levenspiel, O. Chemical reaction engineering. John Wiley & Sons. 3rd ed., 1999
2. Fogler. H. S. Elements of chemical reaction engineering. Pearson Education. 4th ed., 2006
3.Hill, Charles. An introduction to chemical engineering kinetics and reactor design. John Wiley & Sons, 1977.
4. Danckwerts, P. V. Continuous Flow Systems. Distribution of Residence Times. Cambridge, Department of Chemical Engineering, Tennis Court Road, 1952.
5. Lide, D. R. CRC Handbook of Chemistry and Physics.
6. BASMADJIAN, D., *Mass Transfer: Principles and Applications*, pg. 97, CRC Press LLC, Florida (2003)
7. CUSSLER, E. L., *Diffusion Mass Transfer in Fluid Systems*, pg. 127, Cambridge Press, (2009)
8. *Dynamic Help* do COMSOL