

# NONIDEAL FLOW MODELS IN HOMOGENEOUS CHEMICAL REACTORS

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## Summary

For an accurate analysis of the performance of a chemical reactor the following relationships and functions are necessary: reaction rates defining the chemical kinetics, the RTD function of the exit stream from the reactor, the state of aggregation of the fluid (microfluid or macrofluid) and its tendency to coalescence and redispersion while flowing through the reactor as well as earliness and lateness at which mixing occurs and its influence on the final conversion degree. These problems are the subject of research of the discipline named chemical reaction engineering – an intensively developing branch of the chemical engineering.

In this chapter the functions determining the RTD (The density of RTD  $E(t)$  and the cumulative RTD  $F(t)$ ) have been defined and the method of their experimental estimation presented. The role of moments in comparing different RTD curves has been discussed. The nonideal flow models like axially dispersed plug flow model, the tanks in series model and the multiparameter models, which enable the estimation of RTD functions were developed. Special attention has been devoted to explaining the concept of the state of aggregation of the fluid by introducing two limiting cases, i.e. the microfluid and the macrofluid and the mechanisms of intermixing ascribed to them. Finally, the method of calculating the conversion in the exit stream from the reactor has

been demonstrated by using the relationships and functions quoted above.

## 1. Introduction

The ideal flow patterns, i.e. the plug flow and the ideal mixed flow (discussed in *Ideal Models of Reactors*) are widely accepted as very useful and effective tools in the analysis, design and operation of chemical reactors. In the plug flow the fluid elements which entered the reactor vessel at the same moment are moving along parallel streamlines with the same velocity. Thus, the residence time of all fluid elements in the reactor is identical. On the other hand in the mixed flow the mixing phenomena are assumed to be extremely intensive ensuring a complete uniformity of the composition of the fluid and its temperature in the entire vessel. These two ideal flow patterns considerably facilitate the analysis and design of chemical reactors offering straightforward methods of selecting the right type of reactor.

However, in real reactors cases are often encountered where the flow pattern deviates from either of the two limiting ideal flows, and their application in the analysis of chemical reactors can lead to substantial errors. Generally speaking, these deviations can depend on the reactor type, kind of fluid and the characteristics of flow, and are usually caused by the existing stagnant regions in the vessel, by recirculating and bypassing the fluid as well as by mixing phenomena generated by the flow itself (turbulent mixing).

## 2. The Residence Time Distribution (RTD)

From the theoretical point of view the quantitative description of the reaction processes occurring in the reactor could be determined as a result of the simultaneous analysis of the mass, momentum and energy balance equations. The solution of these differential equations would lead to the estimation of the velocity profile and the intensity of mixing phenomena in the reactor. These quantities would then allow us to determine the influence of the hydrodynamic behavior of the fluid on the performance of the chemical reactor with a nonideal flow pattern. Unfortunately such a procedure is in the majority of cases impossible and impractical, even with present-day computers and available numerical methods.

A much simpler approach stems from the fact that the basic information whose knowledge is indispensable for determining the final conversion of a fluid element is its residence time in the reactor. Obviously, the residence time of various fluid elements which entered the vessel at the same moment  $t=0$  will not be the same in a nonideal flow. Therefore, in order to analyze these problems a powerful concept – the residence time distribution of fluid elements in the reactor- has been introduced. This distribution is characteristic of the reactor type and of the flow pattern and enables the estimation of the conversion degree of the reacting mixture leaving the reactor.

The concept of a fluid element, introduced by Danckwerts is a volume of fluid whose size is very small in comparison to the size of the reactor vessel, but contains a sufficient number of molecules to form a continuous system.

The definitions of the RTD functions have been taken from the probability theory. According to this theory the function  $E(t)$  called the density of the RTD determines the value  $E(t)dt$ , i.e. a fraction of the fluid which entered the vessel at the moment  $t = 0$  and leaves it between  $t$  and  $t + dt$ , so

$$E(t)dt = \left[ \begin{array}{l} \text{fraction of fluid leaving} \\ \text{the vessel that has a residence} \\ \text{time } (t, t + dt) \end{array} \right] \quad (1)$$

This value can also be interpreted as the probability that a fluid element which entered the reactor at  $t = 0$  will leave it at the time  $t, t + dt$ . Such a definition of the function  $E(t)$  leads to the following normalizing relationship

$$\int_0^{\infty} E(t)dt = 1 \quad (2)$$

Another kind of function characterizing the fluid stream leaving the vessel is the cumulative RTD –  $F(t)$ . The value of this function for the time  $t$  determines the fraction of the fluid  $F(t)$  which stayed in the reactor for the time shorter than  $t$ . The relationship between these two functions can be obtained from their definitions, i.e.

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

Hence, the function  $F(t)$  takes the following limiting values:

$$F(0) = 0 \quad (4)$$

$$\lim_{t \rightarrow \infty} F(t) = 1 \quad (5)$$

Moreover, from the relationship (3) it follows that

$$\frac{dF(t)}{dt} = E(t) \quad (6)$$

Figures 1 and 2 show the examples of RTD functions  $E(t)$  and  $F(t)$  for the plug flow, ideal mixed flow and nonideal flow.

It has to be noted that the RTD functions  $E(t)$  and  $F(t)$  are valid only for the so called closed – closed vessel where plug flow has been assumed in both the inlet tube and the outlet tube of the vessel.

Very useful in characterizing and comparing the RTD functions are the moments of

these distributions given by the relation

$$\mu_{n,t} = \int_0^{\infty} t^n E(t) dt \quad n = 1, 2 \dots n \quad (7)$$

The first two moments are usually used for the evaluation of the RTD functions. The higher moments like the skewness estimated from experimental RTD curves comprise large errors and therefore are rarely applied in the analysis of the RTD.

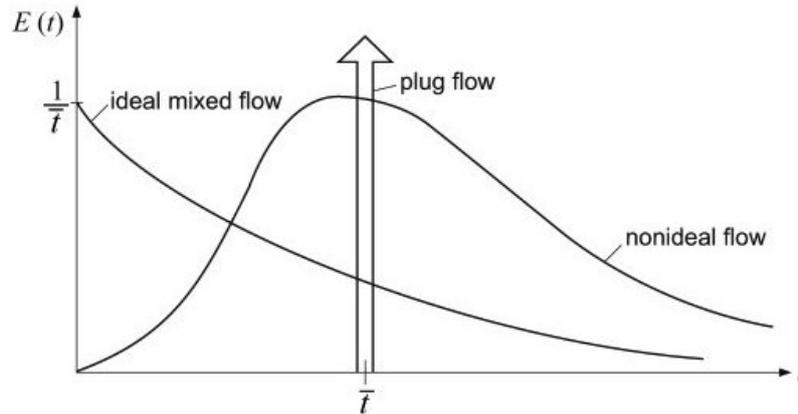


Figure 1. Examples of the function  $E(t)$  for various flow patterns.

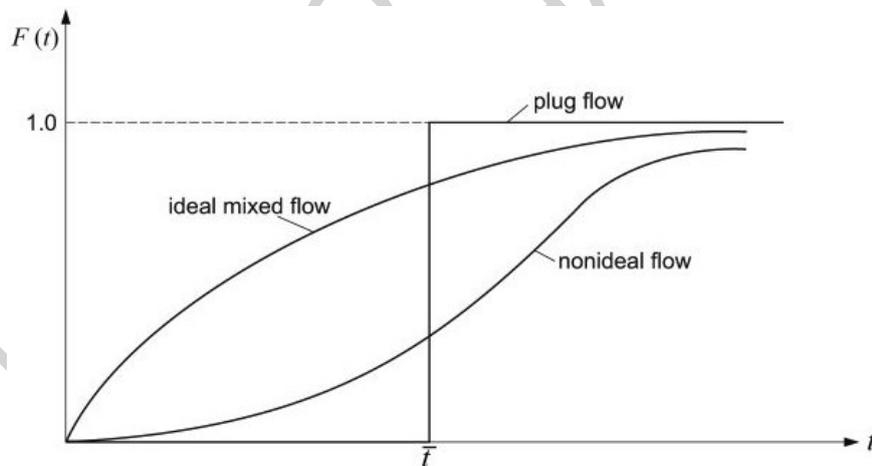


Figure 2. Examples of the function  $F(t)$  for various flow patterns.

The first moment equals the mean residence time in a closed vessel, that means:

$$\mu_{1,t} = \int_0^{\infty} tE(t) dt = \bar{t} = \frac{V}{V^*} \quad (8)$$

An important feature of the RTD very useful in its evaluation is the “width” of the distribution curve. This value is undoubtedly a measure of the intensity of the mixing phenomena. According to the probability theory this “width” can be best defined by the

central second moment with respect to the mean residence time called variance. Thus

$$\sigma_t^2 = \int_0^{\infty} (t - \bar{t})^2 E(t) dt = \int_0^{\infty} t^2 E(t) dt - \bar{t}^2 \quad (9)$$

In comparing different RTD curves it proved convenient to introduce into the foregoing equations the dimensionless time, defined as

$$\Theta = \frac{t}{\bar{t}} \quad (10)$$

Based on the equality

$$E(t) dt = E(\Theta) d\Theta \quad (11)$$

one obtains the following dependence

$$E(\Theta) = \bar{t} E(t) \quad (12)$$

and

$$F(t) = \int_0^t E(t) dt = \int_0^{\Theta} E(\Theta) d\Theta = F(\Theta) \quad (13)$$

Using the dimensionless time the moments (8) and (9) may be written as follows:

$$\mu_{1,\Theta} = \int_0^{\infty} \Theta E(\Theta) d\Theta = 1 \quad (14)$$

and

$$\sigma_{\Theta}^2 = \frac{\sigma_t^2}{\bar{t}^2} = \int_0^{\infty} (\Theta - 1)^2 E(\Theta) d\Theta = \int_0^{\infty} \Theta^2 E(\Theta) d\Theta - 1 \quad (15)$$

A special technique has been developed for determining experimentally the RTD curves called the stimulus – response technique or the tracer technique. In this technique a fixed amount of a tracer substance is introduced into the fluid stream at the inlet into the vessel by means of a strictly specified mode. Monitoring the concentration of the tracer as a function of time at the outlet from the reactor allows us to determine the RTD curve. The appropriately selected tracer should not take part in any process during the flow through the vessel which could cause its consumption (like chemical reaction, absorption or adsorption). Moreover, its amount should not disturb the pattern of flow and change the physical properties of the fluid.

The two following methods of introducing the tracer are generally used in experiments. The first one is the step function where at  $t=0$  the inflowing concentration is changed from one value, usually zero, to another one. The second is a pulse, where a specified amount of tracer is injected in a shortest possible time into the inflowing fluid.

Let us assume that in a general case the tracer is introduced in the form of an exactly defined function  $C_{A0}(t)$ . The function  $C_{A0}(t)$  is transformed during the flow through the vessel according to the RTD function  $E(t)$  characteristic of the flow pattern in the vessel. The monitored concentration at the outlet is then given by  $C_{A1}(t)$  (Figure 3).

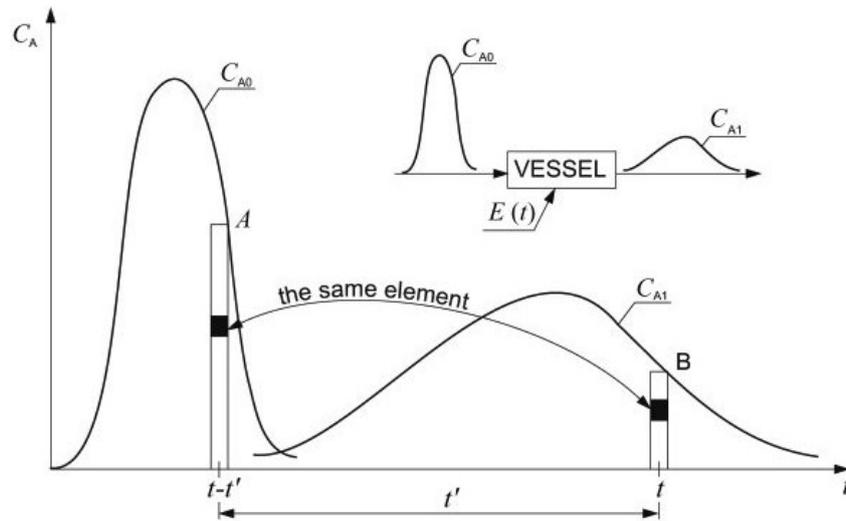


Figure 3. Scheme of a general method of developing the RTD function

The fluid element leaving the vessel at time  $t$  (rectangle B) comprises the fractions determined by the RTD function  $E(t)$  of all fluid elements which entered the vessel over the time period  $[0, t]$ . Therefore, in order to determine the concentration  $C_{A1}(t)$  of the fluid element leaving the vessel we have to add the fractions of all fluid elements which entered into the vessel at time  $t - t'$  and stayed in the vessel for the time  $t'$  (all rectangles A). This sum will be expressed in the limit by means of the convolution integral giving finally the desired relationship between the concentrations

$$C_{A1}(t) = \int_0^t C_{A0}(t-t')E(t')dt' \quad (16)$$

An equivalent form of this relationship is

$$C_{A1}(t) = \int_0^t C_{A0}(t')E(t-t')dt' \quad (17)$$

and applying the usual mathematical notation for the convolution integral one obtains

$$C_{A1} = C_{A0} \times E \quad (18)$$

$$C_{A1} = E \times C_{A0} \quad (19)$$

The simplest mathematical expressions allowing us the experimental determination of the RTD functions are obtained by simulating the inlet tracer injections in the form of the Dirac  $\delta(t)$  function for the pulse and the Heaviside step function  $1(t)$ .

The first function is defined as follows

$$\delta(t - t_0) = \begin{cases} 0, & \text{for } t < t_0 \\ \infty, & \text{for } t = t_0 \\ 0, & \text{for } t > t_0 \end{cases} \quad (20)$$

and the second function as

$$1(t) = \begin{cases} 0, & \text{for } t < 0 \\ 1, & \text{for } t > 0 \end{cases} \quad (21)$$

In the first case a fixed amount of tracer  $n_A$  is injected into the inlet stream of the reactor in an infinitely short time, hence

$$C_{A0}(t') = \frac{n_A}{V^*} \delta(t') \quad (22)$$

Substituting this equality into the Eq.(17) one gets:

$$C_{A1}(t) = \int_0^t \frac{n_A}{V^*} \delta(t') E(t - t') dt' \quad (23)$$

During integration, the function  $\delta(t')$  selects only the value of  $E(t - t')$  for  $t' = 0$ , so

$$C_{A1}(t) = \frac{n_A}{V^*} E(t) \quad (24)$$

Hence, based on the monitored outlet concentration  $C_{A1}(t)$  for the stimulus  $\frac{n_A}{V^*} \delta(t')$  the  $E(t)$  function is obtained as

$$E(t) = \frac{V^*}{n_A} C_{A1}(t) \quad (25)$$

or, in an equivalent form

$$E(t) = \frac{1}{t} \frac{V}{n_A} C_{A1}(t) \quad (26)$$

and in a dimensionless form

$$\bar{t} E(t) = E(\Theta) = \frac{V}{n_A} C_{A1}(t) \quad (27)$$

The quantity  $\frac{n_A}{V}$  can be treated as the initial concentration  $C_{A0}$  formed as a result of an immediate uniform dispersion of the tracer amount  $n_A$  in the whole volume  $V$  of the vessel. Thus,

$$E(\Theta) = \frac{C_{A1}(t)}{C_{A0}} \quad (28)$$

Applying the stimulus in the form of the Heaviside step function the inlet concentration is changed from zero to the value  $C_{A0}$  at the time  $t' = 0$

$$C_{A0}(t') = C_{A0}1(t') \quad (29)$$

and from (17) one obtains

$$C_{A1}(t) = \int_0^t C_{A0}1(t')E(t-t')dt' = C_{A0} \int_0^t E(t)dt = C_{A0}F(t) \quad (30)$$

and, finally

$$F(t) = \int_0^t E(t)dt = \frac{C_{A1}(t)}{C_{A0}} \quad (31)$$

An exact estimation of the amount  $n_A$  injected into the inflowing stream in a shortest possible time may be difficult. This value can then be estimated by monitoring the concentration  $C_{A1}(t)$  in the outlet stream until its disappearance, i.e. theoretically for an infinitely long time

$$n_A = V^* \int_0^{\infty} C_{A1}(t)dt \quad (32)$$

Substituting Eq.(32) into Eq.(25) gives

$$E(t) = \frac{C_{A1}(t)}{\int_0^{\infty} C_{A1}(t) dt} \quad (33)$$

Especially difficult is the estimation of the  $E(t)$  function by applying an arbitrary inlet signal  $C_{A0}(t)$  as, in this case,  $E(t)$  is present implicitly in the convolution integral (17).

In this situation it is most convenient to apply the Laplace transformation of the convolution simultaneously with Borel's theorem. According to this theorem the Laplace transform of the convolution is equal to the product of the Laplace transforms of the original functions forming this convolution

$$\overline{C_{A1}}(s) = \overline{C_{A0}}(s) \overline{E}(s) \quad (34)$$

and hence

$$\overline{E}(s) = \frac{\overline{C_{A1}}(s)}{\overline{C_{A0}}(s)} \quad (35)$$

leading to the RTD function as a Laplace transform  $\overline{E}(s)$ . The next step is the reverse transformation of  $\overline{E}(s)$  to obtain the original function  $E(t)$ .

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### **Biographical Sketch**

**Andrzej Burghardt** was born in 1928 in Warsaw, Poland. He received his B.Sc. in 1952 and finally graduated in Chemical Engineering from the Silesian Technical University, Gliwice, Poland obtaining M.Sc. degree. In 1962 he received his Ph.D. while in 1965 the degree Doctor in Technical Sciences from the same university. In 1971 he was awarded a title of Professor in Technical Sciences by the President of the Republic of Poland while some years later, in 1983, he was elected as a member of the Polish Academy of Sciences. In the years 1987-2003 he was a chairman of the Committee of Chemical Engineering at the Polish Academy of Sciences.

Currently he is a member of the Presidium of the Polish Academy of Sciences and of the Scientific Council at the Ministry of Science and Informatics. He is also an active member of the Working Party on Chemical Reaction Engineering of the European Federation of Chemical Engineering.

In the years 1954-1966 he was engaged at the Silesian Technical University, Gliwice, Poland as an Assistant Professor lecturing in Distillation, Mass Transfer and Chemical Reaction Engineering. Then, in 1966, he moved to the Institute of Chemical Engineering of the Polish Academy of Sciences where he was designated to the post of director holding this post until 2002. His field of research focuses mainly on the theory of mass transfer in multicomponent and multiphase systems as well as on chemical reaction engineering with special interest in dynamics of chemical reactors. He is author and co-author of nearly 200 scientific publications in refereed journals and of following books and chapters in collective editions: *Chemical Reactors' Engineering Vol. I and II, Examples of Reactor Design, Dynamics of Processes in a Porous Catalyst Pellet, Mass Transfer in Multicomponent Systems, Condensation of Multicomponent Mixtures in VDI-Wärmeatlas (Three Ed. in German one in English)*. He is also a member of Editorial Boards in several journals.