

9.2. Residence time distribution measurement in chambered reactor and packed column

9.2.1. Introduction

In the equipment used by the chemical industry, materials are subjected to certain effects (temperature, pressure, physical and chemical effects). The duration of these effects in the various processes is very important. In many cases, good mixing can be detrimental, e.g. during the sterilization of milk, where the temperature must be sufficiently high to kill spores, but the milk can only be subjected to this temperature for a short time to avoid loss of valuable components (vitamins). Thus, rapid heating, short-time high temperature sterilization and rapid cooling are required.

If we were to carry out sterilization in a continuous, stirred tank, results would be unsatisfactory. Good mixing would cause part of the liquid to exit right away, i.e. without sterilization, while other parts would remain subjected to high temperatures in the equipment longer than desired, damaging the vitamins. Therefore, mixed tanks cannot be used in continuous mode, if the material can only reside in the equipment for a definite period of time.

In batch processes, this problem does not exist, because all particles have identical residence time.

In most cases, a uniform residence time would be desirable, when every particle or volume element in the material would traverse the reactor with equal speed on equally long paths (as is the case with plug flow) and fluid elements following each other would not mix. This ideal flow scenario is called **perfect displacement**.

9.2.2. Theoretical background

Mean residence time

In a steady-state equipment, mean residence time can be calculated by the following formula:

$$\bar{t} = \frac{m}{\dot{m}} \quad (9.2-1)$$

where m is the mass of material in the equipment (kg), \dot{m} is the mass of material added to the reactor in a given time (mass flow: kg/s). If the density of the material does not change in the equipment, then based on the above formula:

$$\bar{t} = \frac{V}{\dot{V}} \quad (9.2-2)$$

where V is the volume of fluid in the equipment (m^3), \dot{V} is the volumetric flow (m^3/s).

In a continuous equipment, particles of the feed material can have extremely different residence times, which vary randomly for a given particle. We can only state the probability of the residence time t being between certain limits.

Aim of residence time distribution measurements

The aim is to describe real flow, macroscopic mixing, heat transfer and mass transfer in chemical industry equipment with a mathematical model. The mathematical model allow us to calculate the separation achievable in mass transfer equipment or the conversion in reactors. If the effects of operating parameters on the residence time distribution and the mathematical model are known, optimal operating conditions can be determined, and based on the mathematical model the dynamic behavior of the equipment linked to a controller can be studied.

It is very important that the chosen model contain a mathematical description of all significant hydrodynamic processes, while at the same time having a simple equation and few parameters to be determined empirically.

If the equipment is not functioning properly, the separation is poor or conversion is low, residence time distribution can help determine the cause of inadequate operation. Residence time distribution can detect channel formation (short-circuit), stagnant regions mixing poorly with the main flow and internal recirculation.

Residence time distribution is described by the density function $E(t)$ and the distribution function $F(t)$.

Residence time distribution density function $E(t)$

$E(t') dt$ is equal to the fraction of the mass flow exiting the equipment with residence time between t' and $t' + dt$ (Figure 9.2-1a). The integral of the density function from 0 to ∞ is one.

$$\int_0^{\infty} E(t) dt = 1 \tag{9.2-3}$$

It follows from the definition of the function $E(t)$ that it has a dimension of [1/time]. Multiplying the $E(t)$ function by the mean residence time yields the dimensionless form:

$$E(\mathcal{G}) = \bar{t} E(t) \tag{9.2-4}$$

where $\mathcal{G} = t/\bar{t}$ is the reduced time, relative to the mean residence time.

Residence time distribution function $F(t)$

The value of the distribution function $F(t)$ at time t' gives the fraction of the exiting mass flow that remained in the equipment for a time of t' or shorter (Figure 9.2-1b).

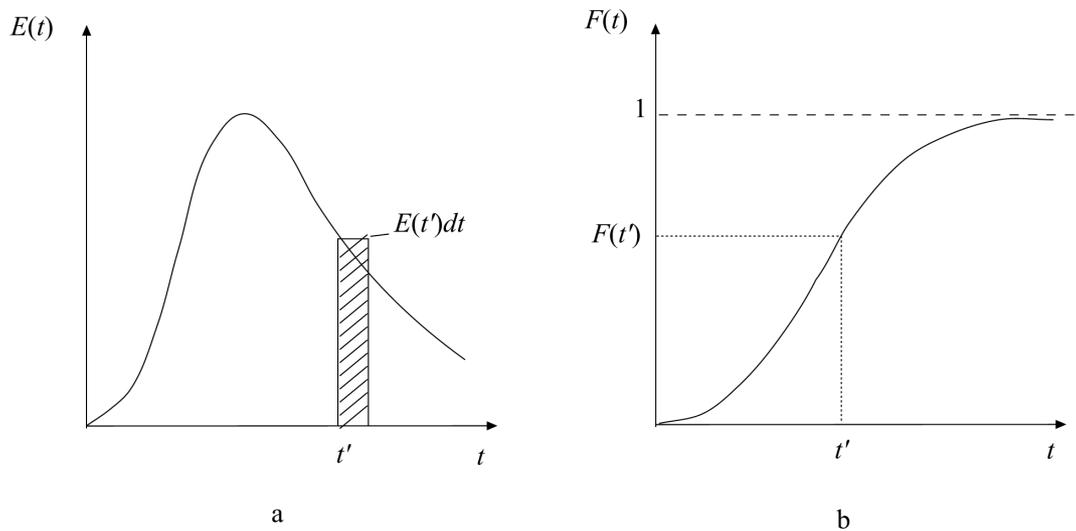


Figure 9.2-1. Residence time distribution functions: a) density; b) distribution

The distribution function is the integral of the density function from 0 to t' .

$$F(t') = \int_0^{t'} E(t) dt \quad (9.2-5)$$

It follows that the distribution function grows monotonously with t and tends to a limit of one as $t \rightarrow \infty$.

Measuring residence time distribution

We will measure the residence time distribution by tracer response analysis. The tracer must be chosen to be a compound that satisfies the following criteria: dissolves only in the phase being examined, does not disturb the flow, passes through the system unchanged (i.e. does not react with material in the equipment, does not become immobilized), its hydrodynamic behavior is similar to the particles of the surrounding phase and its concentration is easily measurable.

The basic concept of residence time distribution methods is creating a concentration disturbance at the inlet of a steady-state equipment and measuring the response signal in the effluent. We only need to consider convective mass transport in the inlet and outlet piping, because the flow rates here are significantly larger than those inside the reactor. This means that no material exits (or is reintroduced into) the equipment via diffusion or turbulent mixing; thus **the system is closed with respect to mixing**.

In a **pulse experiment**, n_0 (mol) amount of tracer is introduced into the equipment over a period of time much shorter than the mean residence time, and the tracer concentration $c(t)$ (mol/m³) is measured in the effluent as a function of time.

The fraction of tracer leaving the reactor between times t and $t + dt$ is equal to $Vc(t)dt/n_0$.

It follows from the above definition of the residence time distribution density function that:

$$E(t)dt = \frac{Vc(t)dt}{n_0} \quad (9.2-6)$$

The amount of tracer introduced needs not be measured, as it can be calculated from the $c(t)$ concentration–time curve:

$$n_0 = \dot{V} \int_0^{\infty} c(t)dt \quad (9.2-7)$$

Substituting this into (9.2-6) yields:

$$E(t) = \frac{c(t)}{\int_0^{\infty} c(t)dt} \quad (9.2-8)$$

Evaluating residence time distribution density curves

The parameters P_i of the mathematical model are determined by fitting the calculated pulse response curve to the experimentally determined curve. The best fit is obtained when the sum of the squared differences between the calculated and experimentally determined points is minimal.

Method of moments

The moment of methods is a faster method for evaluating pulse response curves. The n^{th} initial moment of the residence time distribution density function about the origin ($t = 0$) is defined as

$$(M_n)_t = \int_0^{\infty} t^n E(t)dt \quad (9.2-9)$$

The index t of M_n indicates that its dimension is [timeⁿ]. The first initial moment $(M_1)_t$ is the mean value of the distribution. In a closed system with respect to mixing, $(M_1)_t$ equals the mean residence time. The moment about the mean or center of the distribution is called the **central moment**.

$$(\mu_n)_t = \int_0^{\infty} (t - \bar{t})^n E(t)dt \quad (9.2-10)$$

During the calculations, it is advantageous to use dimensionless moments. Dimensionless moments are defined as:

$$M_n = \frac{(M_n)_t}{(\bar{t})^n} \quad \text{és} \quad \mu_n = \frac{(\mu_n)_t}{(\bar{t})^n} \quad (9.2-11)$$

The width of the density function, i.e. the deviation of residence times around the mean can be characterized by the value of μ_2 . Thus, the second central moment is also called the variance, denoted by σ^2 .

The basic concept of the moment of methods is equating the moments $M_{n,\text{exp}}$ obtained from the measured residence time distribution density curve by numerical integration according to equation (9.2-9) or (9.2-10) with the corresponding theoretical moments $M_n(P_i)_{\text{model}}$ obtained from the model.

$$M_{n,\text{mért}} = M_n(P_i)_{\text{model}} \quad (9.2-12)$$

Solving the equations yields the values of parameters P_i .

Disadvantages of pulse experiments: The end of the pulse response curve cannot be measured precisely, only with large relative error. Due to the factor t^n these errors become especially prevalent for higher moments. Also, it is impossible to attain the upper limit of integration ($t = \infty$).

Because of the aforementioned errors, the method of moments cannot be used to determine whether the chosen model provides an adequate description of the residence time distribution. This can only be determined from comparing the $E(t)$ curves obtained from measurements with those calculated with parameters obtained by the method of moments. If the parameters are independent, then we need to calculate n moments to obtain the values of n parameters. Since moments of order higher than two can only be calculated with increasing imprecision, the moment of methods is mainly used with simple two-parameter models.

Ideal stirred tank

A tank is considered to be ideally stirred if the material fed into it is dispersed uniformly in its entire volume over a period of time much shorter than the mean residence time. In practice, if the stirred material is not too viscous, this requirement can easily be fulfilled. In ideal stirring, the concentration in the tank is uniform and equal to that of the outlet stream.

Instationary mass balance for the tracer:

$$\dot{V}(c_{be} - c_{ki}) = V \frac{dc_{ki}}{dt} \quad (9.2-13)$$

The residence time distribution density function can be derived as:

$$E(t) = \frac{dF(t)}{dt} = \frac{1}{\bar{t}} \exp(-t/\bar{t}) \quad (9.2-14)$$

Residence time distribution for cascade of tanks (cell model)

A system of serially coupled ideally stirred tanks of equal volume (the so-called *cell* or *cascade model*) was the first model used to mathematically describe the residence time distribution.

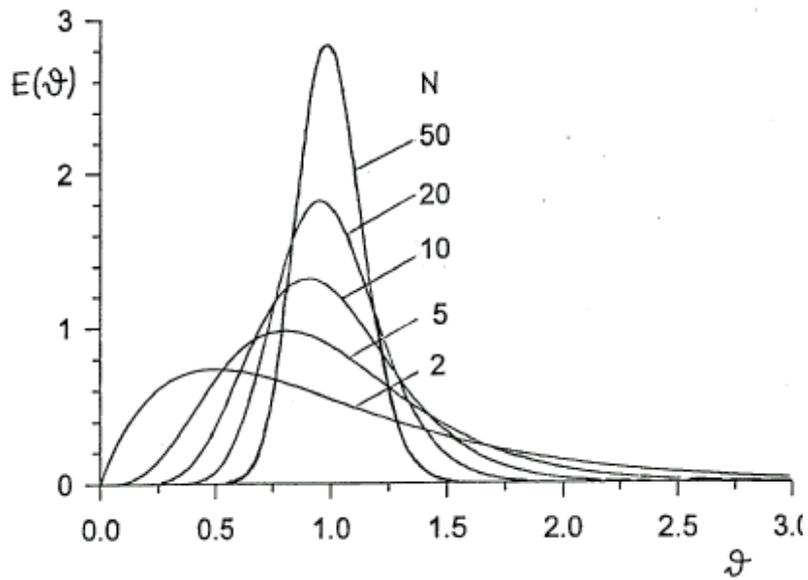


Figure 9.2-2. Residence time distribution density function for a cascade of N tanks

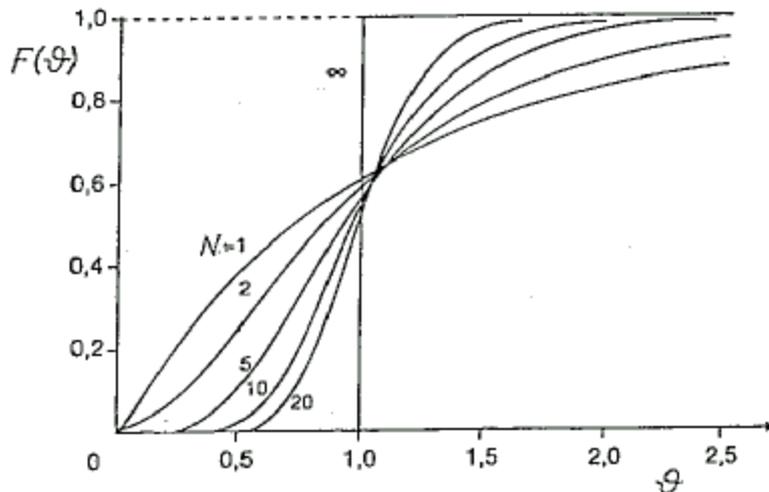


Figure 9.2-3. Residence time distribution function for a system of serially coupled tanks

The dimensionless residence time distribution density function of the cell model:

$$E(\vartheta) = \frac{N(N\vartheta)^{N-1}}{(N-1)!} \exp(-N\vartheta) \quad (9.2-15)$$

where N is the number of ideally stirred tanks (cells), $\vartheta = t/\bar{t}$ is the reduced time relative to the mean residence time, \bar{t} is the mean residence time for the whole system.

The dimensionless variance:

$$\sigma^2 = 1/N \quad (9.2-16)$$

The cell model can be used for any multi-stage equipment where adequate structural design prevents mixing between the stages: e.g. the residence time distribution in a concurrent bubbling tower divided into stages by perforated plates can be adequately described using this model.

When calculating the residence time distribution density function, if the cell number (N) calculated from σ^2 is not a whole number, the Γ -function must be substituted into the denominator of equation (9.2-16) instead of $(N-1)!$ (Γ -model).

$$\Gamma(n) = \int_0^{\infty} x^{n-1} \exp(-x) dx \quad (9.2-17)$$

if N is a positive whole number, $\Gamma(N) = (N-1)!$

Recirculation model

This model considers the equipment as consisting of N ideally stirred cells of equal volume. The strength of recirculation between adjacent cells is described by the recirculation parameter γ : $\gamma = \dot{V}_{rec} / \dot{V}$, the quotient of the recirculation stream (\dot{V}_{rec}) and the feed stream (\dot{V}). The model is shown schematically in the following figure.

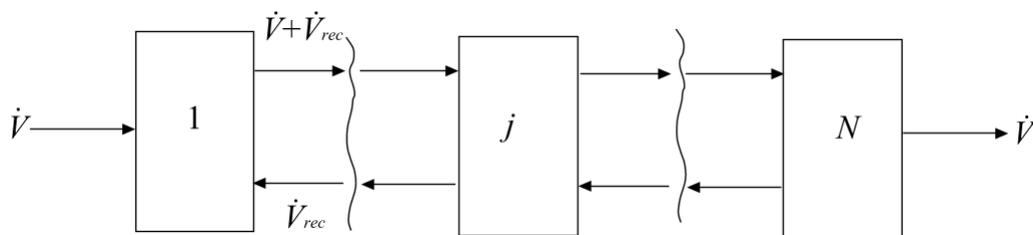


Figure 9.2-4. Recirculation model

Equation of the residence time distribution density function [1]:

$$E(\vartheta) = 2N\gamma \cdot a^{N+1} \sum_{j=1}^N A_j \cdot \exp(-z_j \vartheta) \quad (9.2-18)$$

where

$$A_j = (-1)^{j+1} \frac{\sin^2 \psi_j}{1 + z_j}$$

$$z_j = N \left[1 + 2\gamma (1 - a \cdot \cos \psi_j) \right]$$

$$a = \left(\frac{1 + \gamma}{\gamma} \right)^{1/2}$$

ψ_j is the j^{th} root of the following transcendental equation:

$$\psi_j (N + 1) + 2 \operatorname{arctg} \left(\frac{\sin \psi_j}{a - \cos \psi_j} \right) = j\pi$$

Variance is given by:

$$\sigma^2 = \frac{1 + 2\gamma}{N} - \frac{2\gamma(1 + \gamma)}{N^2} \left[1 - \left(\frac{\gamma}{1 + \gamma} \right)^N \right] \quad (9.2-19)$$

Diffusion model

Instationary mass balance of the tracer in a volume element of the equipment [2]:

$$\frac{\partial c_i}{\partial t} = -\operatorname{div}(\mathbf{v}c_i) + \operatorname{div}(D \operatorname{grad} c_i) \quad (9.2-20)$$

where D is the dispersion (also known as macroscopic mixing or turbulent diffusion) factor (m^2/s), \mathbf{v} is the velocity vector (m/s).

Changes in the concentration in a unit period of time are due to convection $[-\operatorname{div}(\mathbf{v}c_i)]$, or diffusion $[\operatorname{div}(D \operatorname{grad} c_i)]$. Equation (9.2-20) is the basic formula of the diffusion model (also known as the dispersion model).

Let us apply the above equation to a cylindrical equipment of large diameter.

$$D_{rad} \left[\frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} \right] + D_{ax} \frac{\partial^2 c}{\partial l^2} - v \frac{\partial c}{\partial l} = \frac{\partial c}{\partial t} \quad (9.2-21)$$

where D_{rad} and D_{ax} are the radial and axial mixing factors, r is the radial space coordinate (m), l is the length coordinate (m), v is the velocity of the axial plug flow.

- The above equation is valid if the flow inside the equipment is turbulent (in this case the axial velocity profile of the fluid is very close to that in plug flow),
- radial and axial mixing factors are constant,
- radial velocity is zero.

In a cylindrical pipe of small diameter, if the flow is turbulent, radial mixing causes the concentration to be uniform in a given cross-section of the equipment. This means that equation (9.2-21) is further simplified:

$$D_{ax} \frac{\partial^2 c}{\partial l^2} - v \frac{\partial c}{\partial l} = \frac{\partial c}{\partial t} \quad (9.2-22)$$

This is the transport equation of the *one-dimensional diffusion model*.

Let us multiply both sides of equation (9.2-22) by the mean residence time ($\bar{t} = L/v$) and divide by the inlet concentration c_{in} of the tracer (the input signal amplitude).

$$\frac{D_{ax}}{vL} \frac{\partial^2 C}{\partial z^2} - \frac{\partial C}{\partial z} = \frac{\partial C}{\partial \theta} \quad (9.2-23)$$

where L is the length of the equipment (m), $z = l/L$ is the dimensionless space coordinate, $C = c/c_{be}$. The dimensionless group (vL/D_{ax}) is referred to in literature as the PÉCLET number (Pe). For perfect macroscopic mixing $D_{ax}/vL = \infty$, for perfect displacement $D_{ax}/vL = 0$.

If the diameter of the inlet and outlet piping is significantly smaller than the diameter of the equipment, then mixing (dispersion) will only occur in the equipment and we can assume ideal displacement in the piping (closed system with respect to mixing). Accordingly, the boundary conditions for the beginning and end of the equipment are:

$$vc_0 = vc|_{l=0} - D_{ax} \left. \frac{\partial c}{\partial l} \right|_{l=0} \quad \text{and} \quad \left. \frac{\partial c}{\partial l} \right|_{l=L} = 0 \quad (9.2-24)$$

The LANGMUIR–DANCKWERTS boundary conditions for the beginning of the equipment only hold true for mixed systems (e.g. mechanically stirred towers). This boundary condition states that a discontinuity in concentration exists at $z = 0$ even in steady state.

The one-dimensional diffusion model was used successfully to describe the residence time distribution of various pieces of continuous equipment in chemical engineering (packed absorber, liquid-liquid and solid-liquid extractor, bubbling column reactor, ball mill, etc.).

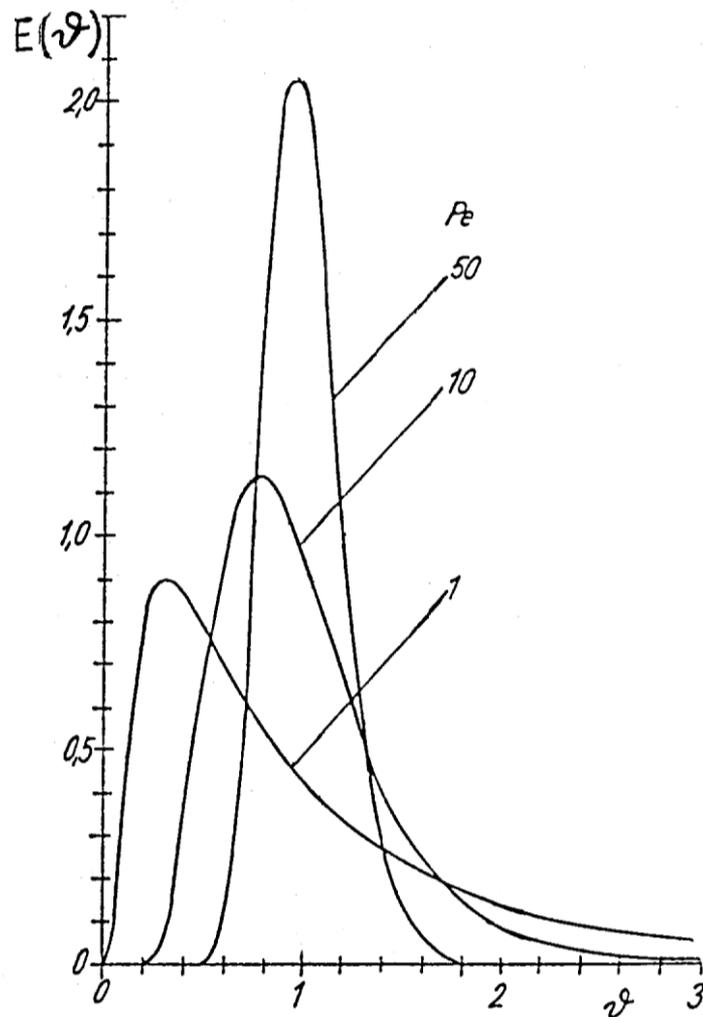


Figure 9.2-5. Residence time distribution density function of the one-dimensional diffusion model, if the system is closed at both ends with respect to mixing

The residence time distribution density function of the *one-dimensional diffusion model* closed at both ends with respect to mixing [3]:

$$E(\theta) = \frac{2}{Pe} \exp\left(\frac{Pe}{2}\right) \sum_{j=1}^{\infty} B_j \cdot \exp(-m_j \theta) \quad (9.2-25)$$

where

$$B_j = (-1)^{j+1} \frac{\varphi_j^2}{1 + m_j}$$

$$m_j = \frac{\varphi_j^2}{Pe} + \frac{Pe}{4}$$

$$\varphi_j \text{ is the } j^{\text{th}} \text{ root of the transcendental equation } \operatorname{ctg} \varphi_j = \frac{\varphi_j}{Pe} - \frac{Pe}{4\varphi_j}.$$

$$\text{Variance: } \sigma^2 = \frac{2}{Pe} \left(1 - \frac{1}{Pe} [1 - \exp(-Pe)] \right) \quad (9.2-26)$$

9.2.3. Description and operation of the equipment

Figure 9.2-6. shows the operational scheme of the experimental equipment. Distilled water is fed into the equipment from a feed tank on the upper level. Volumetric flow rate is measured by a rotameter. Depending on the valve settings, either the packed column or the chambered reactor can be operated.

The **chamber reactor** is a steel tube with a diameter of 58,5 mm and a length of 200 mm, divided into 5 chambers (cells) of equal volume by metallic rings on spacer rods. The internal diameter of the stationary rings is 18,5 mm. Chamber mixing is provided by flat mixing discs 40 mm in diameter, mounted on an axle running parallel to the reactor tube. Mixing speed can be continuously adjusted in the interval 0-1200 1/min. Liquid is fed into the reactor at the bottom and exits at the top. Tracer (sodium chloride solution, concentration 300 g/l) is introduced into the reactor through the syringe at the bottom of the reactor. A pair of electrodes mounted at the top of the reactor measure conductivity, which is proportional to the concentration. The reactor is encased by a thermostating jacket.

The **packed column** is a glass tube with a diameter of 35 mm, and a length of 910 mm. The packing (spheres, Raschig-rings etc.) are changed systematically. In the column, liquid flows from the bottom to the top. The salt solution is introduced via a syringe. The response signal is measured by a conductometric cell at the top of the column.

The built-in measurement cells are connected to a conductometer displaying the conductivity, which is proportional to the concentration. The voltage output signal of the conductometer is sent through an interface to a computerized measurement and data collection system. From the start of the measurement, the computer measures the output signal of the conductometer at user-specified intervals, and after analog/digital signal conversion displays it in the range of 0 to 5. At the

end of the measurement, the data can be saved in a file.

Measurement instructions

Fill the feed tank with distilled water. Start liquid feed. It is recommended to wash the equipment with distilled water before beginning the experiment. Set the volumetric flow rate (5-15 l/h) and the rotation speed of the chamber reactor mixer (500-900 1/min) specified by the instructor. Inject the tracer and at the same time, start the data collection. Measurement and data acquisition is done by the program LABDAS. A detailed instruction manual is available next to the computer. Please carry out the experiment according to the instructions. If the response signal approaches the base signal (the first number on the screen at the beginning of the measurement) stop the measurement and, after entering the other parameters, save the data. The instructor specifies the number of measurements to be performed.

9.2.4. Evaluating the results

The measured pulse response can be evaluated with the residence time distribution program TIE. You will find a detailed instruction manual for the program next to the computer.

Select your measurements from the folder “adatfile”. Evaluate every data series using the method of moments. Using formulas (9.2-16), (9.2-19) and (9.2-26) the program calculates the effective cell number (N), the recirculation coefficient (g) and the Peclet number (Pe). The recirculation coefficient is not applicable to the packed column. Compare the density function ($E(\theta)$) obtained from the measured pulse response with the theoretical curves from the mixing models (Γ -model, recirculation model, diffusion model). Use the parameters obtained from the method of moments (N , g , Pe) for the calculations. The graph will show the sum of the squared differences between the measured and calculated curves (dimensionless!). Based on these values, choose the mathematical model that adequately describes the macroscopic mixing inside the equipment.

Recommended complimentary assignment: For the model that adequately describes the mixing, find the parameter of the curve that best approximates the residence time distribution by minimizing the sum of the squared differences between the experimental and calculated curves.

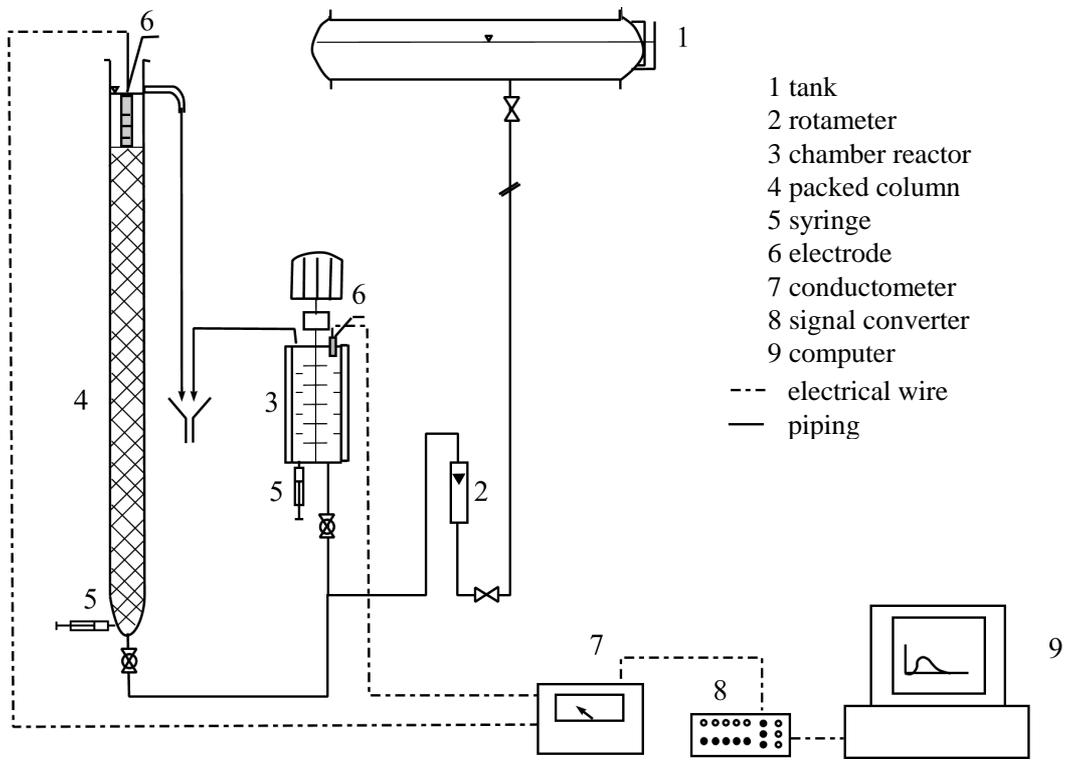


Figure 9.2-6. Experimental equipment for determining residence time distribution

Measurement record

Equipment: chamber reactor/packed column

Mixer speed: 1/min

Feed volumetric flow rate: dm^3/h

Mean residence time: s

Model	Parameter	Sum of squared differences
Γ -model	N :	
Recirculation	g :	
Diffusion	Pe :	

Remarks:

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