

RE9: Residence Time Distribution

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1 Introduction and Objective

In this experiment the students will study the *residence time* in a real non-reactive system by measuring the concentration of an injected tracer *methylene blue* before and after a reactor. The learning objectives of the exercise are the following:

- The students should be able to translate measured quantities into a *residence time distribution* (RTD).
- The students should know how the residence time in a real reactor differs from that of an ideal *plug flow reactor* (PFR).
- The students should know how to create figures of presentable quality.
- The students should be able to apply regression techniques to calibrate equipment based on experimental data.

In chemical reactor engineering the *residence time* describes the time spent inside a reactor, i.e. the time at which a molecule enters the reactor subtracted from the time at which it leaves the reactor. For a steady state ideal *plug flow reactor* (PFR) model the fluid is assumed to only flow in one direction. All volume elements can hereby be viewed as pistons being pushed forward by the volume elements behind as illustrated in Figure 1. For this reactor, the velocity remains constant for all its pistons, meaning that all molecules share the same residence time, i.e. they spend the same amount of time inside the reactor. In this experiment, the student will study a real reactor where back-mixing is allowed. As a result of this, the molecules will have different residence times. The distribution of these residence times is called the *residence time distribution* (RTD).

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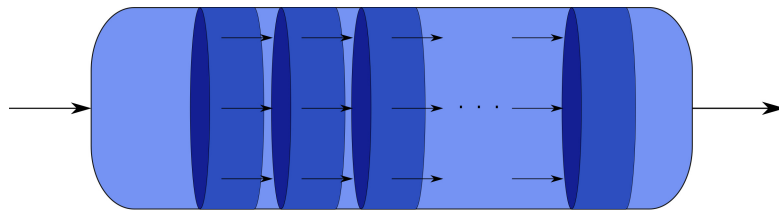


Figure 1: Plug flow reactor (PFR) with control volumes regarded as pistons pushed forward by the piston behind.

2 Background Theory

The following section is based on the theory of Kashid [1] explaining the principles of the *residence time distribution* (RTD) and how it can be determined. The RTD for a real reactor can be found by injecting a fluid that is distinguishable from the bulk fluid. In this experiment a *methylene blue* solution is applied as an optical tracer. The RTD can be visualised as a *probability density distribution* $E(t)$ calculated following Equation (1).

$$E(t) = \frac{\hat{n}}{n_0} = \frac{qc(t)}{\int_0^\infty qc(t)dt} = \frac{c(t)}{\int_0^\infty c(t)dt} \quad (1)$$

Here n_0 is the total molar amount of injected tracer, and \hat{n} the molar flow of tracer out of the reactor. The concentration of tracer $c(t)$ leaving the reactor at time t can be introduced considering the volumetric flow-rate q in the second term. The final equation is obtained by applying a constant pump rate, allowing the constant flow-rate q to be taken out of the integral. The distribution $E(t)$ denotes the probability that a tracer molecule spends a time t inside the reactor. As time t approaches infinity all tracer molecules must eventually have left the reactor. The probability of a molecule having left the reactor between time zero and infinity must hereby be equal to 1 as shown in Equation (2).

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

Figure 2 further illustrates the principles of $E(t)$. At time t equal to t_1 , 79% of the injected tracer molecules have left the reactor, with 21% still remaining inside. This means that 79% of the tracer molecules have a residence time of less than t_1 seconds. For an ideal PFR model, all molecules have a residence time equal to the statistical mean (average) of the RTD. However, since all molecules have the same residence time there doesn't really exist any residence time *distribution* for an ideal PFR model. The statistical moment of order j is given by Equation (3).

$$\mu_j = \int_0^\infty t^j E(t)dt \quad (3)$$

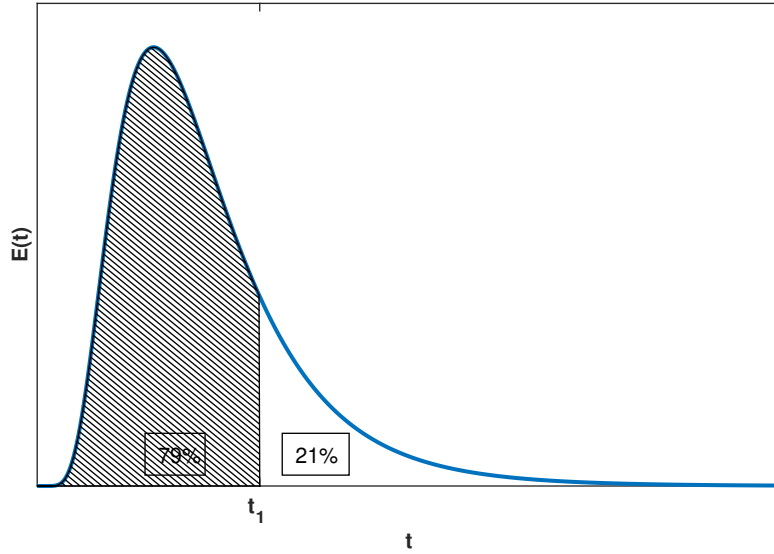


Figure 2: Generic residence time distribution (RTD) $E(t)$. At t equal to t_1 , 79% of the injected tracer molecules have left the reactor.

The *mean residence time* can hereby be calculated by Equation (4). Further moments may also be employed to gain further information on the distribution, such as the standard deviation and skewness by the second and third statistical moments respectively.

$$\bar{t} = \mu_1 = \int_0^{\infty} tE(t)dt \quad (4)$$

The above derivations are based on three assumptions. Firstly, the system is assumed to be *non-reactive* with molecules independent of each other. For reactive systems, Equation (1) doesn't apply as the total amount of injected molecules n_0 is not conserved. Figure 3 illustrates how n_0 moles of tracer travel through an ideal PFR with the same amount exiting the reactor at time t equal to t_N . The real reactor is similar, but with molecules having different residence times, yielding an RTD.

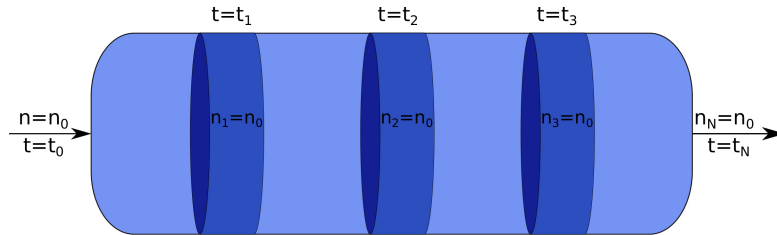


Figure 3: Number of moles of tracer molecules travelling through an ideal plug flow reactor (PFR).

The second assumption includes *steady state* flow conditions. The assumption is justified

by a well controlled pump rate. This provides a constant volumetric flow rate q , and the ideal PFR residence time τ can be calculated by Equation (5), where V_r is the reactor volume.

$$\tau = \frac{V_r}{q} \quad (5)$$

The final assumption includes a constant density, justified by the fact that the system is non-reactive with a constant temperature.

The integrals in Equation (1), (2) and (4) may be evaluated with the numerical method preferred by the student. Typical suggestions are the method of Riemann sums, the method of trapezoids, or Simpson's method. The former method should not be employed due to its numerical inaccuracy. The two latter are given respectively by Equation (6) and (7).

$$\int_0^\infty f(t)dt = \sum_{i=0}^{i=N} A_i = \sum_{i=0}^{i=N} \frac{f_{i+1} + f_i}{2} (t_{i+1} - t_i) \quad (6)$$

$$\int_0^\infty f(t)dt = \frac{h}{3}(f_0 + 4f_1 + 2f_2 + \dots + 4f_{2i-1} + 2f_{2i} + \dots + 4f_{2N-1} + f_{2N}) \quad (7)$$

Here h equal to $(t_{2N} - t_0)/2N$ is the equidistant spacing of each interval. For data sets with unequal spacing, the method of trapezoids may be employed due to its simplicity. Hint: MATLAB has a function called `trapz`. Call it on (x, y) -pairs as such: `trapz(x, y)`. For Python, NumPy has implemented a trapezoidal rule. The following code will integrate $x = [1, 2, 3]$ and $y = [1, 4, 9]$ and store the integral in `I`:

```
import numpy as np
x = [1, 2, 3]
y = [1, 4, 9]
I = np.trapz(y, x)
```

3 Experimental

The student will prepare three 250 mL solutions of methylene blue with different concentrations. This is done by dissolving the appropriate amount of salt in de-ionized water. For preparation, volumetric flasks should be used.

Hint: It is nearly impossible to weight in the exact amount of methylene blue. Weight in an approximate amount, write down the exact amount, and calculate the obtained solution's concentration.

Concentrated solutions of methylene blue are disposed in the waste container marked with **organic solvents with halogene**. Extremely diluted solutions ($\ll 1$ mg/L) may be disposed in the sink.

The experimental setup is illustrated in Figure 4. De-ionized water is pumped from the first tank, through two light sensors and a reactor, and into the waste tank. The optical tracer solution is injected with a syringe (ca 1 mL) between the pump and the first light sensor as a pulse. The injection should be quick so that all molecules enter the system at approximately the same time. **Important:** The first sensor is used to set the sample starting time t_0 defined as the time of the maximum response of the first sensor. The registered time for both sensors should further be corrected such that t_0 equals time zero. The reactor consists of a long tube filled with static mixers (metal disturbing the flow patterns). After a while, the tracer will come out, and the concentration is measured by the second sensor to find the RTD. All quantities are sampled at their own time interval, and the measurement output data file will include pump rate as well as top and bottom sensor voltage with three separate time samples.

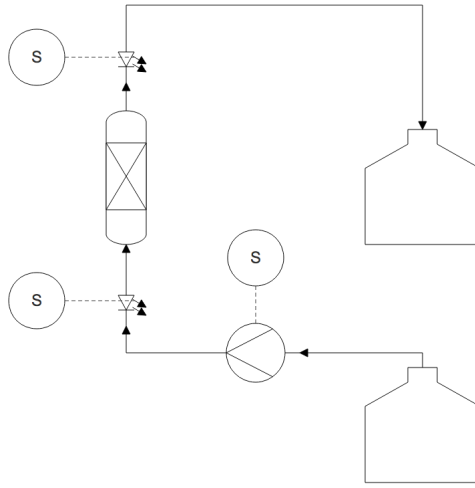


Figure 4: Experimental setup with de-ionized water being pumped from the first tank through a reactor and into the waste tank. The tracer is injected after the pump and before the first sensor.

$$\Delta U_T(t) = \beta_T \times c(t) \quad (8)$$

$$\Delta U_B(t) = K_B \left(1 - \exp \left(- \frac{c(t)}{\tau_{p,B}} \right) \right) \quad (9)$$

$$\Delta U_i(t) = U_{i, idle} - U_i(t) \quad (10)$$

The light sensors have been calibrated so that the measured voltage for the top (T) and bottom (B) sensor can be mapped over to concentration following Equation (8) and (9) respectively. Here $\Delta U_i(t)$ is the difference in measured voltage $U_i(t)$ from the idle resting value $U_{i, idle}$ (for pure de-ionized water) for sensor i , calculated by Equation (10). The calibration of $\Delta U_T(t)$ and $\Delta U_B(t)$ with respect to tracer concentration following Equation (8) and (9) is shown in Figure 5. The top sensor will never see concentrations larger than the plotted domain, because of the mixing in the reactor. This is why a linear fit is sufficient. The linearly fitted parameter β_T is determined to be 0.0730 with a coefficient of determination of R^2 of 0.917. The R^2 -value is a measure, ranging from 0 to 1, of how well the model predicts the data. The two fitted parameters K_B and $\tau_{p,B}$ in (9) are listed with their 95% confidence intervals in Table 1.

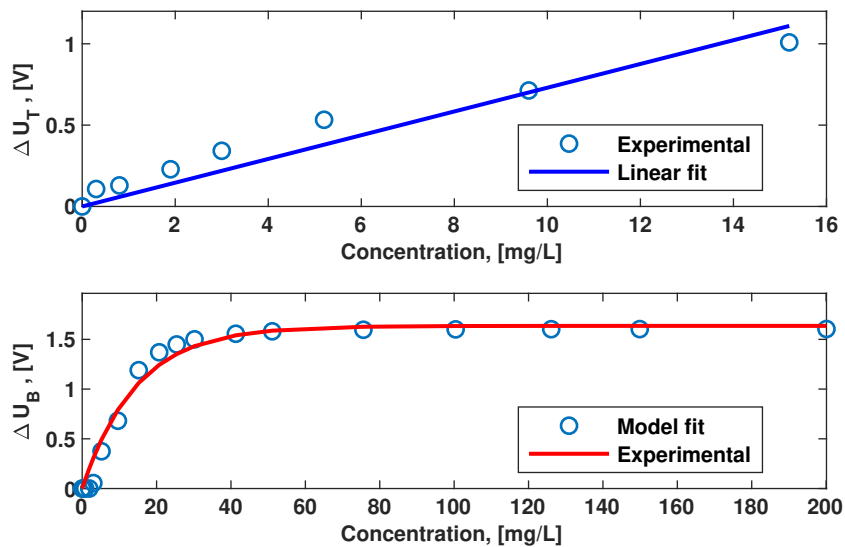


Figure 5: Calibration of $\Delta U_T(t)$ and $\Delta U_B(t)$ with respect to tracer concentration following Equation (8) and (9). The model fit is the full line, and the experimental data are O-markers. Note that they are plotted for different concentrations.

Table 1: Calibrated parameters for bottom sensor with 95% confidence intervals following Equation (9).

Parameter	Value	Lower bound	Upper bound
K_B	1.636	1.542	1.730
$\tau_{p,B}$	14.50	11.34	17.65

Figure 6 shows a typical voltage measurement for the top sensor. When the tracer enters

the sensor, less light passes through the fluid, and the measured voltage drops. When the tracer concentration drops, the voltage slowly rises again. **Important:** Make sure to let the voltage return to the idle resting value $U_{i,idle}$ before ending a measurement to allow all tracer molecules to leave the reactor. The idle resting values $U_{T,idle}$ and $U_{B,idle}$ for the top and bottom sensors have been measured to 4.5695 and 4.9012 V respectively.

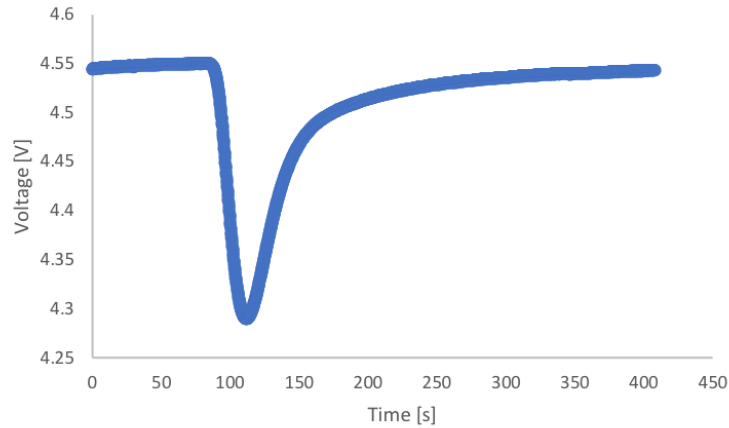


Figure 6: Typical top sensor voltage measurement following tracer pulse injection. When the tracer enters the sensor, less light passed through the fluid, and the voltage drops. The voltage rises slowly as the concentration drops.

4 Work Plan

The students are expected to deliver a work plan to the lab assistant (Björn Baumgarten) before being allowed to enter the lab. It is to be submitted at least 3 days in advance. The work plan is submitted to bjorn.baumgarten@ntnu.no, and should contain the following: introduction, objectives and a procedure with calculations to obtain the desired concentrations of methylene blue. Include the use of personal protection equipment as indicated in the Risk Assessment in your work plan.

Include waste handling into your work plan. Following waste needs to be considered: Surplus methylene blue solution (concentration: as prepared), Mixture of methylene blue solution and water from experiments (concentration: $\ll 1$ mg/l).

5 Tasks and Report

The students shall perform the following tasks in the lab:

1. Prepare three different methylene blue solutions (250 mL) of known concentrations.

Use concentrations between 10-150 mg/L. The weight is precise to the first decimal (with respect to mg).

2. Sample one injection for three different pump rates in the range 400-1200 RPM for all three concentrations (9 samples in total). Use the same three pump rates for all concentrations.
3. Perform a pump calibration. Fill a measuring cylinder with a known volume V_{cal} of de-ionized water. Start the pump and register the time t_{cal} it takes to consume the known volume. Use the same three pump rates as in the previous measurements. Take two samples for each pump rate (6 samples in total). The volumetric flow rate q can be calculated as V_{cal}/t_{cal} and applied for the pump calibration.

Due to the Corona-situation, it is required that equipment is only handled by one person before disinfection. To avoid disinfection of equipment during the experiments, one student should handle the lab computer. The other tasks require gloves and are less critical, but still, no equipment should be touched by multiple persons. After finishing lab, all the equipment and surfaces need to be cleaned and disinfected.

In addition to the above lab tasks, the students should perform calculations and visualise results in figures/tables of presentable quality. The results and reflections should be presented in a *short report* including:

1. Plot and compare the response $c(t)$ of the top and bottom sensor for one of the samples. Are they different? Why or why not? Describe the flow of the tracer. How does it move through the system after the pulse injection?
2. Plot the nine RTDs ($E(t)$) in three figures, each at constant concentration with different pump rates. Also plot the nine RTDs at constant pump rates with different concentrations. Compare the two cases (constant concentration and constant pump rate).
3. Validate that the RTDs integrate to one over the entire domain.
4. Calibrate the pump so it maps pump rate (in RPM) to volumetric flow rate q . The type of regression analysis (linear, polynomial, exponential, nonlinear) is chosen by the student.
5. Calculate the mean residence time \bar{t} and compare it to the ideal PFR residence time τ . Are they different? Why or why not? Hint: The volume of the reactor V_r is 44 mL and q at the different pump rates can be calculated from the pump calibration curve.

All calculations should be included in the appendix of the report. However, it is not necessary to show the same calculations more than once. Remember to include your references. Having a theoretical description without any references means you have come up with this yourself. If this is not true, it is both dishonest and disrespectful to not

credit those who did.

The half-way report is to be handed in one week after the experiment was conducted. This is the only feedback the student will receive, and therefore it should be the same quality as a normal report. After feedback from the lab assistant is received, the students have one additional week until the final report is to be handed in.

References

- [1] M. N. Kashid, “Microstructured devices for chemical processing,” 2014.