1 Introduction and Objective

In this experiment the students will measure the residence time of a real non-reactive system by measuring the concentration on an injected pulse of methylene blue 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.
- The students should know how the residence time of 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 the obtained 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 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 is expected to study a
real reactor where backmixing is allowed. As a result of this backmixing, the molecules will have different residence times, and the distribution of these residence times is called the residence time distribution.

Figure 1: A plug flow reactor (PFR) where control volumes are regarded as pistons pushed forward by the piston behind.

2 Background Theory

This section is based on the theory of Kashid [1], and will focus on elaborating the term residence time distribution (RTD), how it can be found, and what role it plays. The RTD can be found for a reactor by injecting a fluid that is distinguishable from the continuous fluid flow. The injected fluid is called the tracer, and some examples of such tracers are ink or methylene blue. The injected amount of tracer, \( n_0 \), will move through the reactor, and the amount leaving the reactor is measured. A typical measurement of the RTD is the statistical probability density distribution, \( E(t) \). This distribution denotes the probability that a fraction of the injected amount, \( n_0 \), has left the reactor at time \( t \).

\[
E(t) = \frac{\dot{n}}{n_0} = \frac{qc(t)}{\int_0^\infty qc(t)dt} = \frac{c(t)}{\int_0^\infty c(t)dt}
\] (1)

In (1), \( \dot{n} \) denotes the molar flow of tracer out of the reactor, \( q \) is the volumetric flow rate and \( c(t) \) is the concentration of tracer leaving the reactor at time \( t \). The last equality comes from the constant pump speed, which allows \( q \) to be taken out of the integral. After a long time has passed (\( t \to \infty \)) all tracer must eventually have left. This means that the probability of all tracer having left equals 1. In mathematical notation this means that:

\[
\int_0^\infty E(t)dt = 1.
\] (2)

In Figure 2, this is further emphasized. After \( t > t_1 \), 79% of the injected molecules have left the reactor, while 21% of them still remain inside. When
all tracer has left, 79% of the molecules spent less than $t_1$ seconds in the reactor.

![Figure 2: A generic residence time distribution, $E(t)$](image)

When $t > t_1$, 79% of the injected molecules have left the reactor.

For an ideal PFR model, the residence time is equal to the statistical mean (average) of the distribution. Hence, no distribution exists for the ideal PFR. The statistical moment of order $j$ is given by:

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

resulting in the mean residence time

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

Further moments may also be employed to gain further information on the distribution, such as the standard deviation, and skewness. The second and third statistical moment, respectively, yields the desired information. This model derivation has some assumptions and requirements. Three assumptions have been made: a) the system is non-reactive, b) the flow conditions are at steady state, and c) the density is constant. The experiment is of interest for a reactive system, however, the experiment must be carried out
for non-reactive systems only, where the molecules may be assumed independent of each other. Infinitesimally small subvolumes of tracer may be observed in the reactor, and their concentration may be related to the residence time. For reactive systems, it does not make any sense to relate the molar flow out of the system to the amount injected. For those systems, (2) is violated. In Figure 3, the number of moles of tracer travel through the PFR and after $t = \tau = V/q$, the same number of moles come out on the other side. A real reactor is similar, but the molecules will have different residence times, yielding an RTD. This is not true for reactive systems, as the number of moles are not conserved. In assumption b), the pump is well controlled, and the flow rate is therefore at steady state. The last of the assumptions is justified by the fact that the system is non-reactive and the temperature of the system is constant.

![Figure 3](image.png)

Figure 3: The figure depicts how the number of moles travel through the PFR and out on the other side.

Finally, the integrals in (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 of them is discouraged, and should not be employed, due to its numerical inaccuracy. The two latter are given respectively as follows:

$$
\int_0^\infty f(t)dt = \sum_{i=0}^{i=N} A_i = \sum_{i=0}^{i=N} \frac{f_{i+1} + f_i}{2} (t_{i+1} - t_i), \\
(5)
$$

$$
\int_0^\infty f(t)dt = \frac{h}{3} (f_0 + 4f_1 + 2f_2 + ... + 4f_{2i-1} + 2f_{2i} + ... + 4f_{2N-1} + f_{2N}) \\
(6)
$$

Here $h = \frac{t_2N - t_0}{2N}$ is the equidistant spacing in each interval. For unequal spacing, 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 $I$: 

4
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, all with different concentrations. This is done by measuring an appropriate amount of the salt, and then diluting with de-ionized water. Due to the colouring properties of methylene blue, nitrile gloves is to be worn when handling the compound. Safety goggles and lab coat shall also be worn at all times as the lab is used for other experiments simultaneously. Concentrated solutions of methylene blue are put in the waste container marked with organic solvents with halogene. Extremely diluted solutions (≪ 1 mg L⁻¹) may be poured in the sink. The lab experiment is to be conducted at the setup seen in Figure 4.

Figure 4: The experimental setup is depicted in the figure. The first tank is filled with de-ionized water, and pumped through a reactor and into the waste tank. Tracer is injected after the pump and before the first sensor, and voltages are measured for both the pump and the two sensors.
As seen in the figure, de-ionized water is pumped from the first tank, through two light sensors and a reactor, and into the waste tank. Tracer is injected between the pump and the first light sensor as a pulse. The injection should be quick to ensure that all molecules start to move simultaneously. The reactor consists of a long tube with static mixers (metal disturbing the flow patterns) inside. After a while, the tracer will come out, and the concentration is measured to find the RTD.

All sampled quantities are sampled at their own time interval. Therefore, three different time samples, two voltage samples and one pump speed sample exist. Even though the light sensors measure voltage, they have been calibrated so that their response can be mapped over to concentration:

\[
\Delta U_T = \beta_T c
\]

\[
\Delta U_B = K_B \left( 1 - \exp\left( -\frac{c}{\tau_{p,B}} \right) \right)
\]

where \( \Delta U_i \) is the difference in voltage between de-ionized water and tracer solution for sensor \( i \) (\( \Delta U_i = U_{i,idle} - U_i \)). For a visual representation of what this involves, see Figure 5. After the tracer is injected, less light passes through the fluid, and as a result the voltage drops. When the concentration drops due to being diluted by the water pumped through, the voltage slowly rises again. Important: The idle resting values for the sensors in de-ionized water are \( U_{T,idle} = 4.545 \) and \( U_{B,idle} = 4.898 \) for top and bottom sensors,
respectively. The linearly fitted parameter, $\beta_T$, for the top sensor is given as $\beta_T = 0.0730$ with a coefficient of determination of $R^2 = 0.917$. The $R^2$-value is a measure of how well the model predicts the data. It ranges from 0 to 1, and higher is better. The top sensor will never see concentrations larger than the domain plotted, because of the mixing in the reactor. This is why a linear fit is sufficient. The two fitted parameters in (7b), $K_B$ and $\tau_{p,B}$ are listed with their 95% confidence intervals in Table 1. The behavior of the voltage delta with respect to concentration is shown along with the model fit in Figure 6.

Table 1: Calibrated parameters for bottom sensor with 95% confidence intervals. The parameters are related to (7b).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Lower bound</th>
<th>Upper bound</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_B$</td>
<td>1.636</td>
<td>1.542</td>
<td>1.730</td>
</tr>
<tr>
<td>$\tau_{p,B}$</td>
<td>14.50</td>
<td>11.34</td>
<td>17.65</td>
</tr>
</tbody>
</table>

Figure 6: Voltage delta as a function of concentration. The model fit is the full line, and the experimental data are O-markers. The top sensor is in the upper subfigure, and the bottom sensor is the lower subfigure. Note that they are plotted for different concentrations.
4 Work Plan

The students are expected to deliver a work plan to the lab assistant (Ask Lysne) before being allowed to enter the lab. It is to be submitted at least 48 hours in advance. The work plan is submitted to ask.lysne@ntnu.no, and it should contain the following: introduction and objectives, procedure with calculations to obtain desired concentrations of methylene blue and a risk assessment containing both the risks related to methylene blue as well as safety measures to avoid these risks.

5 Tasks and Report

At the lab, the student shall perform the following tasks

1. Prepare three different, known concentrations of methylene blue. Use concentrations between 10-150 mg L$^{-1}$. The weight is precise to the first decimal.

2. Sample one injection for three different pump speeds in the range 400-1200 RPM for all three concentrations. Be consistent and use the same three pump speeds.

3. Take a beaker or similar and fill it with a known volume, $V$, of de-ionized water. Pump this through for the same pump speeds and time how long it takes for the pump to consume it. This is used to find the volumetric flow rate in order to calibrate the pump ($q = V/t_{measured}$). Take two samples for each pump speed (6 samples in total).

   It is advisable to wait until the top sensor has reached its resting value for de-ionized water (see text above Figure 5) before ending the sample. After the student is done with the above tasks, he/she has all results needed. In addition to these lab tasks, the student should do calculations, create figures and do reflections which are to be included in the report. These involve

   1. Compare the response of the first sensor to the second. Are they different? Why or why not?

   2. Describe the flow pattern of the tracer. How does it move through system from injection to the second sensor?

   3. Plot nine RTDs in three figures. Each figure should be at constant concentration and different pump speeds. Also do the opposite: nine
RTDs at constant pump speed and different concentrations. Compare the two cases (constant concentration and constant pump speed).

4. Validate that a chosen RTD integrates to one over the entire domain.

5. Calibrate the pump so it maps pump speed to fluid volumetric flow rate. The type of regression (linear, polynomial, exponential, nonlinear) is chosen by the student.

6. Check the mean residence time, $\bar{t}$, and compare it to the PFR residence time $\tau = V/q$. Are they different? Why or why not? Hint: The volume of the reactor is 44 mL and $q$ is known from before.

All calculations should be included in the appendix of the report, however it is not necessary to show the same calculation 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 student has one additional week until the final report is to be handed in.

References