



**MEASURING AND MODELLING OF RESIDENCE TIME DISTRIBUTIONS IN
MIXER-SETTLER REACTORS**

Lappeenranta–Lahti University of Technology LUT

Master's Programme in Chemical Engineering, Master's Thesis

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ABSTRACT

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Measuring and modelling of residence time distributions in mixer-settler reactors

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Process optimization through residence time distribution provides impactful information about flow mechanics inside of a reactor without heavy computational modelling. Mixer-settler, containing a stirred tank reactor and two phases would lead to an incredibly complex system computationally, and information this detailed is often unnecessary. Therefore mixer-settler performance through hydrodynamics can be analysed from a pilot scale model by calculating residence time distribution using tracer tests, as was done in this Thesis.

Previous studies on the same topic conducted on mixer-settler systems are scarce and they have not been conducted in a scale this small, but aqueous phase residence time distributions were formed through conductivity measurements over time. No studies were found that analysed organic phase residence time distribution (RTD) from a mixer settler system, and best method to measure organic phase RTD is by using radioactive tracers.

Aqueous phase tracer tests were carefully planned out, and pulse tests experimented with various volume flows. Exit time curves were successfully formed that were used to estimate performance of the reactor and to fit ideal and nonideal models that would describe the data.

Operating conditions were found where mixer closely followed a model of an ideal CSTR, while phases still completely separate at settler side.

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Viipymäaikajakaumien mittaaminen ja mallintaminen mixer-settler reaktoreille

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Prosessin optimointi viipymäaikajakauman kautta antaa hyödyllistä tietoa reaktorin sisäisistä virtauksista ilman monimutkaista laskennallista mallintamista. Mixer-settler, joka sisältää sekoitussäiliöreaktorin ja kaksi faasia, johtaisi laskennallisesti kohtuuttoman monimutkaiseen järjestelmään, ja näin yksityiskohtaiset tiedot ovat usein tarpeettomia. Siksi mixer-settlerin suorituskykyä voidaan analysoida hydrodynamiikan avulla pilottimallin avulla laskemalla viipymäaikajakauma merkkiainekokeiden avulla, kuten tässä opinnäytetyössä tehtiin.

Aiempiä samasta aiheesta tehtyjä mixer-settler-järjestelmiä koskevia tutkimuksia on vähän, eikä niitä ole tehty näin pienessä mittakaavassa, mutta vesifaasin viipymäaikajakaumat muodostettiin johtokyky mittauksilla avulla ajan kuluessa. Aiempiä tutkimuksia, joissa analysoidaan orgaanisen faasin viipymäaikajakaumaa sekoitin erottaja järjestelmästä ei löytynyt, ja paras menetelmä orgaanisen faasin viipymäaikajakauman mittaamiseen olisi radioaktiivisten merkkiaineiden käyttö.

Vesifaasin merkkiainekokeet suunniteltiin huolellisesti, ja pulssikokeilla kokeiltiin erilaisia tilavuusvirtoja. Poistumisaikakäyrät muodostettiin onnistuneesti, joita voitiin käyttää reaktorin suorituskyvyn arvioimiseen ja ideaalisten ja epäideaalisten mallien sovittamiseen.

Löydettiin toimintaolosuhteet, joissa sekoitin toimi lähes ideaalisen CSTR:n mallin mukaisesti, ja faasit pystyttiin edelleen erottamaan toisistaan erottimen puolella.

NOMENCLATURE

Roman

C	concentration	[mol/L or g/L]
$E(t)$	dimensional residence time distribution	[1/s]
$E(\theta)$	dimensionless residence time distribution	
$F(t)$	cumulative residence time distribution	
M	amount or substance of tracer	[mol or g]
m	number of convolutions, an integer	
n	number of reactors	
q	volume flow of recycle flow	[L/h]
Q	volume flow	[L/h]
R	Recycle ratio, Q/q	
t	time	[s]
T_n	time constant, $V_n / q(1+R)$	[s]
V	volume	[L]
V_n	volume of a single stirred tank	[L]

Greek

$\Gamma(t)$	gamma function	
θ	dimensionless residence time, t/τ	
κ	conductivity	[$\mu\text{S}/\text{cm}$]
τ	mean residence time, Q/V	[s^{-1}]

Lower index

<i>B</i>	bypass
<i>D</i>	dead volume
<i>R</i>	reactor

Abbreviations

CFD	Computational Fluid Dynamics
CSTR	Continuous Stirred Tank Reactor
HRT	Hydro Retention Time
PFR	Plug Flow Reactor
RTD	Residence Time Distribution
TIS	Tanks-In-Series

Table of contents

Abstract

1	Introduction	8
2	Residence time distribution	10
2.1	Tracer experiments	12
2.1.1	Pulse test	12
2.1.2	Step tracer test.....	14
3	Flow models	15
3.1	Tanks in series model.....	16
3.2	Non-integer n in CSTR cascade model.....	19
3.3	n amount of CSTRs in series with recycle:.....	23
3.4	Non-integer n with recycle stream	25
4	Experimental setup	28
4.1	Choosing the tracer for RTD experiments	30
4.2	Conductivity data logger	32
4.3	Feed pumps used	33
4.4	Power unit for mixer adjustment.....	34
4.5	Linearity of conductivity curve.....	35
4.6	Density measurement of the phases used.....	36
5	Experimental methods	37
5.1	Conducting tracer test	38
5.2	Placement of the conductivity probes	39
6	Two phase RTD experiments	43
6.1	Aqueous phase RTD	43
6.2	Organic phase RTD.....	44
6.3	Analysis method for organic RTD.....	45
7	Results and discussion.....	46
7.1	Results from 1-phase experiments	46
7.2	Flow model fitted to 1-phase data.....	49
7.3	Results from 2-phase RTD measurements.....	53

7.4	Model fitted to the 2-phase aqueous phase data.....	54
8	Conclusions	57
	References.....	58

1 Introduction

Process intensification is seen as one of the most important topics in modern day chemical engineering. One of the four process intensification principles include “Give each molecule the same processing experience” with an aim to produce ideal reaction conditions through heating, mixing and reactor flow mechanics (Van Gerven, Stankiewicz, 2009). In this work, residence time distribution is utilized to measure and model parameters according to this principle.

Residence time distribution (RTD) can be defined as a probability distribution of time that a molecule spends in a unit operation or reactor. RTD is widely used for process optimization, scaling-up and energy saving, since relatively simple experiments provide information what happens internally in a reactor (Shivani et al., 2022).

Liquid-liquid extraction is in nature a complex hydrodynamic system, that makes both modelling and measuring of RTD difficult (Aminian, 1998). CFD models can be used to obtain complete understanding of flow mechanics in the system, but usually simpler mathematical models provide adequate information about flow mechanics in the system (Tibbitt, 2002).

There are numerous ways to measure residence time distributions for CSTRs and PFRs and there are comprehensive models that can be used describe their non-ideal behavior. Residence time distributions are studied by tracer tests, either with a pulse or a step tracer (Levenspiel, 1999). From pulse tests an exit time curve $E(t)$ can be formed from calculated residence time for the flow, which is used to fit different models with a computational software such as MATLAB. Cumulative curve known as $F(t)$ is calculated from integrating $E(t)$ or directly from a normalized step tracer data (Levenspiel, 1999).

Most common non-ideal models are bypass flow, dead volume and tanks-in-series model (Fogler, 2006). Bypass flow describes a portion of the tracer flows a ‘shortcut’ through the system and is seen as an early sharp spike at the start of exit time curve (Ingham et al., 2007). Dead or stagnant volume means a certain volume of the tank is not mixing properly and remains stagnant, it lowers the effective volume of the reactor and some tracer can get trapped in it and slowly seeps out resulting in a long tail in exit time curve (Ingham et al., 2007).

Tanks-in-series model is used to describe magnitude of back mixing that happens in a reactor. This is done by splitting total volume into n number of smaller reactors in parallel, that add up to same volume as the real CSTR. Utilizing gamma function a non-integer n can be used to fine tune the amount of back mixing or calculate bypass flow with values $n < 1$ (Toson, Doshi & Jajcevic, 2019). These all three models are studied in this Thesis to describe the behavior of single- and two-phase systems in a bench-scale industrial-type mixer-settler cascade.

2 Residence time distribution

Material that runs through a PFR or CSTR reactor in steady-state can flow endless different routes out of the reactor. This creates a distribution that displays the emphasis where most of the material leaves and how long it takes for the last particles to exit the system (Kiadehi, 2019). Main use of RTD is to estimate conversions or concentrations for reactors in use or still under design, and problem diagnostics in reactor flow dynamics (Fogler, 2006).

These two problems are linked into each other since poor reactor design results into too short reaction times and low conversions, or too long reaction times and increase in by-products especially for selective reactions (Adams, 2021).

Residence time distribution can be formed from an experimental data or calculated theoretically and its shape and length gives a lot of information about performance of a reactor. Two main functions are exit time distribution known as $E(t)$, and cumulative distribution known as $F(t)$ (Levenspiel, 1999). Ideal exit time curve is a descending curve, that cuts y-axis in Q/V_R which is calculated residence time τ , where V_R is the volume of the reactor (Levenspiel, 1999).

$$E(t) = \frac{1}{\tau} e^{-t/\tau} \quad (1)$$

where τ space time, 1/s
 t time, s

$$F(t) = 1 - e^{-\frac{t}{\tau}} \quad (2)$$

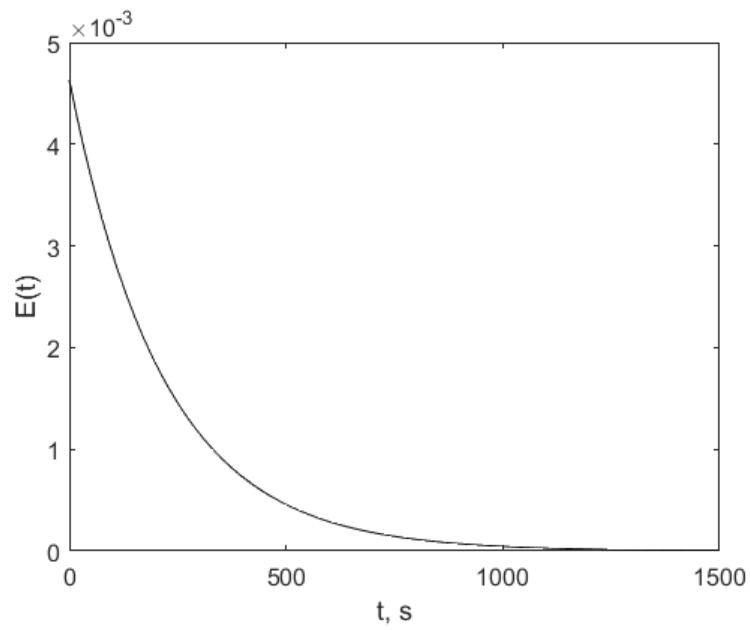


Figure 1. Example of an exit time curve $E(t)$ for ideal CSTR reactor

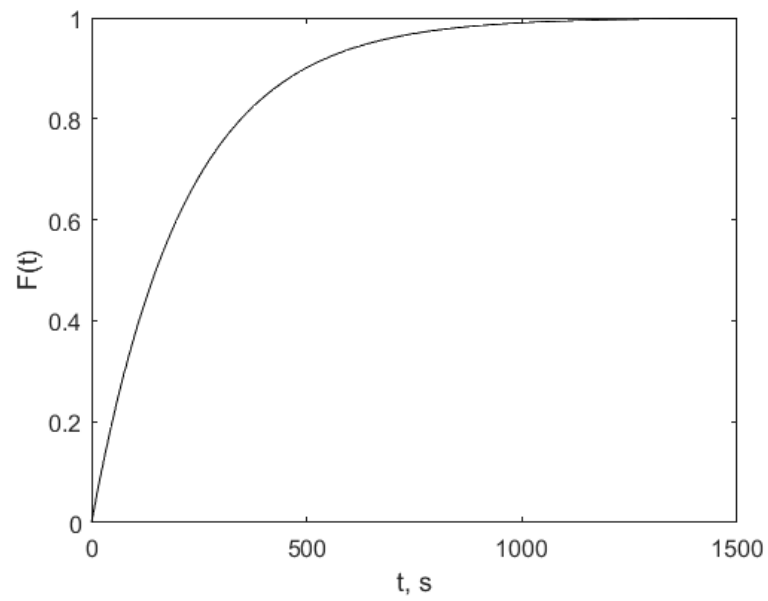


Figure 2. Example of a cumulative residence time distribution $F(t)$ for ideal CSTR

2.1 Tracer experiments

To measure residence distribution time from a reactor, inert tracer solution is fed to inflow and its concentration measured from the outflow (Adams, 2021). Tracer solution can be fed as a pulse or as a step and the resulting output curve is compared to ideal model (Fig 1 & 2).

Most important factors for a successful RTD test are the choice of tracer and the detection limit of analysis method used. The tracer should be easily detected and measured quantities should add up to total amount of tracer injected (Polymerisationstechnik, 2010). From the way the curve differs from an ideal model, early conclusions can be made about what non-ideal behavior should be looked further into.

Mixer was of interest in our case, so tracer experiments were conducted in this Thesis to search for optimal operating conditions where mixer would function close to an ideal CSTR, and on the other hand to yield the highest possible throughput

2.1.1 Pulse test

Theory of a pulse test is that a tracer pulse is introduced into the reactor feed in a short amount of time, and tracer exiting the reactor is measured (Fig 3). Pulse tests require only small amounts of tracer and are popular for their simplicity and cheap cost to conduct (Fogler, 2006).

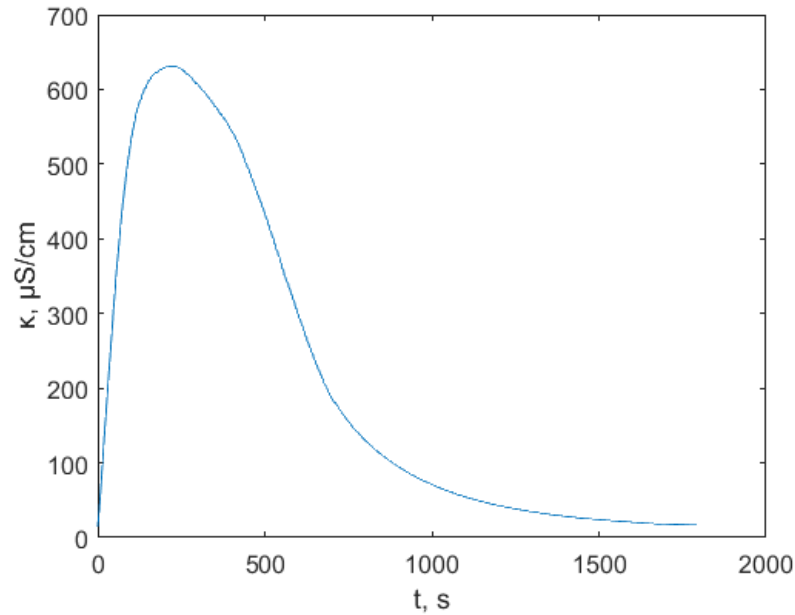


Figure 3. Example of a pulse test, where conductivity is measured over time

To form an exit time $E(t)$ from the pulse experiment data, measured curve is first changed into concentration curve (Fogler, 2006). From the obtained concentration curve, exit time can be calculated by following equation:

$$E = \frac{C_{pulse}}{M/Q} \quad (3)$$

where	C_{pulse}	Tracer quantity, mol/L or g/L
	M	Amount of substance or mass of tracer injected, mol or g
	Q	Volume flow, L/h

Concentration curve from conductivity data requires very accurate measures, since probes must be precisely calibrated with temperature of fluid taken into account, and also mass and concentration of the injected pulse has to be exactly known. Accurate temperature reading is essential since altering the solution temperature by 1 °C can change the conductivity reading by up to 5% (Connelly, 2017).

A simplified method to calculate $E(t)$ assumes that when operating in lower conductivity levels, conductivity increases with concentration linearly. Then the data can be normalized

between 0 and 1 and divided by mean residence time to obtain exit time data curve (Levenspiel, 1999). This reduces the key parameters in data handling to only two, reactor volume and feed volume flow.

$$E(t) = \frac{\kappa_{normalized}}{\tau} \quad (4)$$

where κ conductivity, $\mu\text{S}/\text{cm}$

Ideal CSTR exit time model intercepts y-axis at $1/\tau$ and area under the curve should add up to 1, similarly to a distribution curve the area shows percentage of the material that has exited the reactor.

2.1.2 Step tracer test

Step input is a cumulative curve of exit time curve obtained by integrating E-curve over time: (Levenspiel, 1999)

$$F = \int_0^t E dt \quad (5)$$

It displays percentage of tracer that has left the system over time, and after certain amount of t it reaches 1 indicating 100% of the injected tracer has exited the system (Fogler, 2006).

Step test is conducted by starting a feed of tracer into the reactor inlet and measuring the increase of tracer concentration into its steady-state. Step tracer experiment is easy to carry out and interpret, but it provides less information and expenses will increase quickly if tracer material used is expensive. Larger scale step tests can require tens of liters of tracer material to achieve equilibrium point (Levenspiel, 1999).

3 Flow models

Basic flow models for a CSTR and PFR rarely describe reactors in real life, and these equations have been improved further by other researchers for more complex flow models (Roussinova, Kresta, 2007). Equations provided by these studies are used to find the flow model that best describes the experimental data.

Bypass flow and dead volume are the simplest models to describe non-ideal behaviour for a reactor. In dead volumes case, fraction of the dead volume is removed from total reactor volume which leads to decrease of the mean residence time τ (Fogler, 2006).

$$\tau_D = \frac{(V_R - V_D)}{Q} \rightarrow \tau_D < \tau \quad (6)$$

where	τ_D	Residence time when dead volume is present, h ⁻¹
	V_R	Volume of reactor, L
	V_D	Dead volume, L

For bypass flow, fraction of the material entering to a vessel flows straight to outlet with very little reaction time. Exiting the vessel earlier than designed causes the effective residence time, which means that (Fogler, 2006).

$$\tau_B = \frac{V_R}{(Q - Q_B)} \rightarrow \tau_B > \tau \quad (7)$$

where	τ_B	Residence time when bypassing is present, h ⁻¹
	Q_B	Bypassing volume flow, L/h

When bypass and dead volume percentage are both set as 30%, it gives following results (Fig 4) when compared to ideal CSTR curve. Bypass fraction intercepts y-axis lower than ideal model describing a fraction of material exiting the system at $t=0$. Dead volume shows a higher concentration at $t=0$ since the effective volume of a reactor is smaller, and therefore

hydro retention time (HRT) is also lower so tracer exits the system faster than in an ideal reactor.

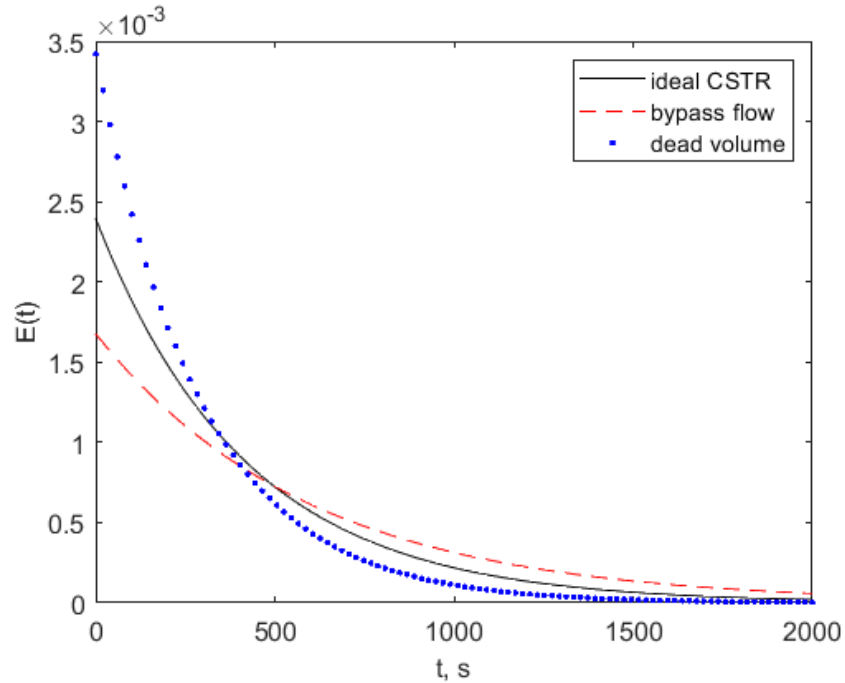


Figure 4. Effect of bypass and dead volume to RTD exit time curve

3.1 Tanks in series model

CSTR cascade is a model used to describe imperfect back mixing. Main principle is that the reactor is divided into n number of CSTRs, where each has the same volume and residence time of τ/n (Fu et al., 1971).

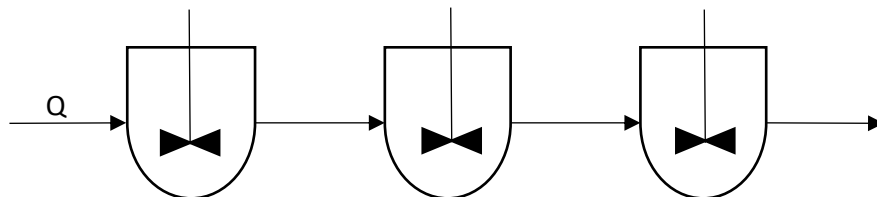


Figure 5. CSTR-in-series model

$$E(t) = \frac{t^{n-1}}{(n-1)!} \left(\frac{n}{\tau}\right)^n \exp\left(-\frac{t n}{\tau}\right) \quad (8)$$

where n number of reactors
 t time, h

Each reactor has a volume of V_R/n which is total reactor volume V_R divided by amount of reactors n , where n can be any positive integer (Fig 6). When $n = 1$ the equation reduces to an equation for ideal CSTR model (Levenspiel, 1999).

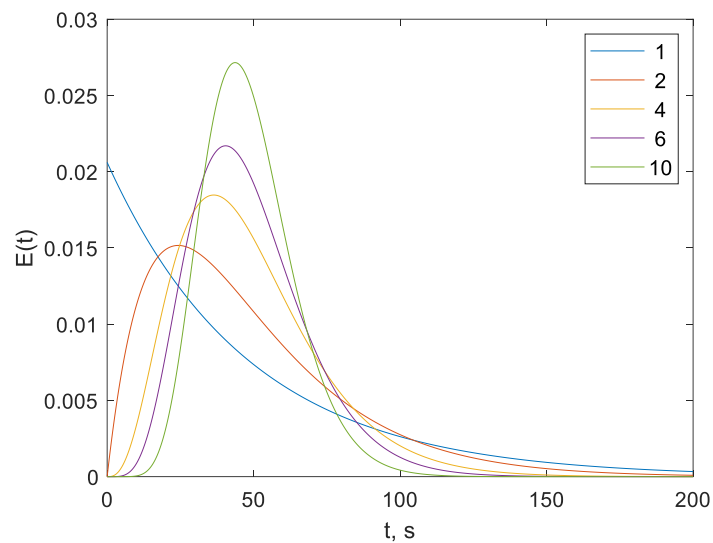


Figure 6. Example of different lengths of CSTR cascades exit time curves over time

When $n \rightarrow \infty$, CSTR cascade model turns into a model of ideal PFR that forms at the mean residence time Q/V (Fig 7) (Levenspiel, 1999).

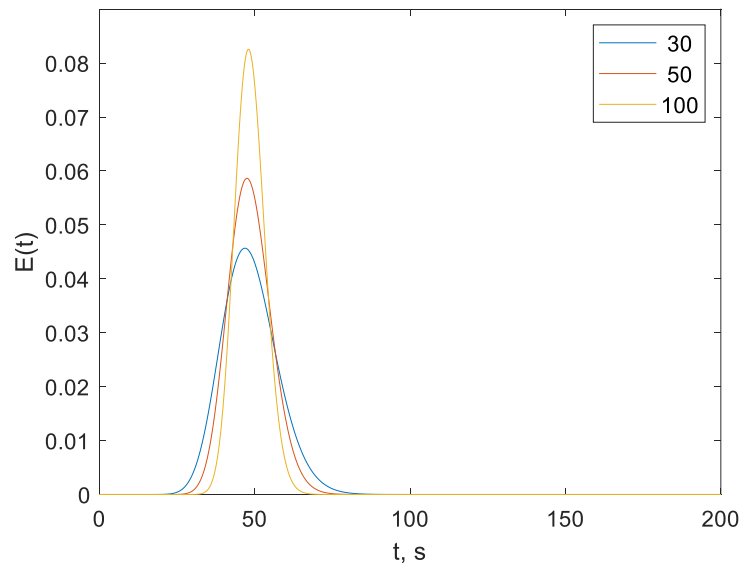


Figure 7. CSTR cascade turns into ideal PFR as the n value nears infinity

When CSTR cascade model is applied to $F(t)$ curve, increasing n value makes resulting curve become steeper and when n nears infinity, cumulative curve becomes a vertical line describing an ideal PFR (Fig 8) (Toson, Doshi & Jajcevic, 2019).

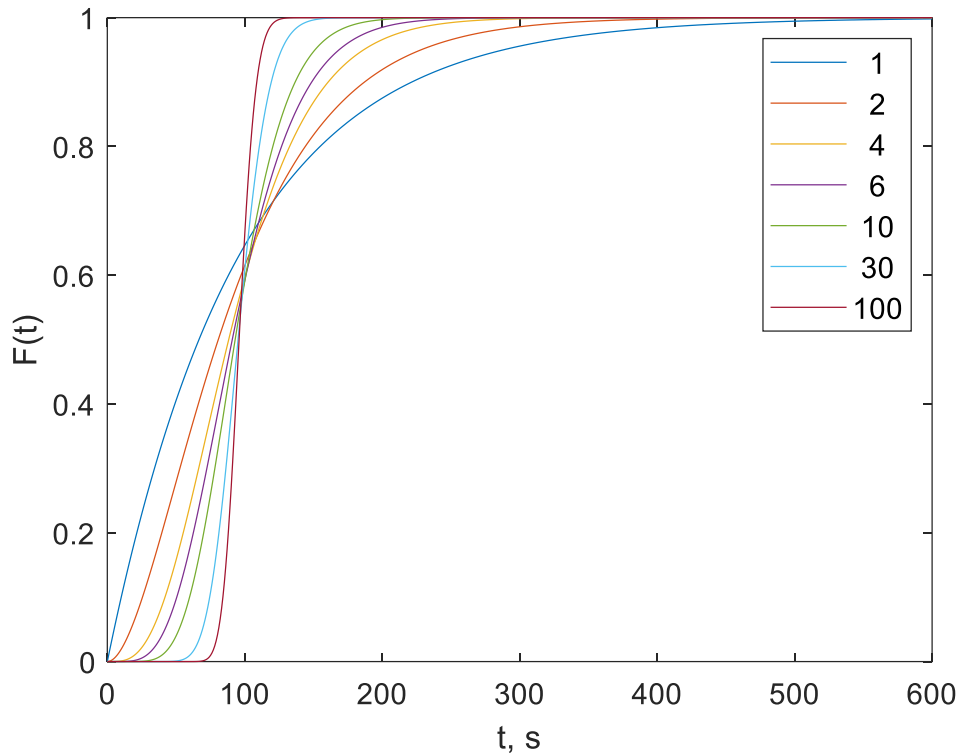


Figure 8. Cumulative RTD curves for different lengths of CSTR cascades

3.2 Non-integer n in CSTR cascade model

Equation (6) proposed by MacMullin and Weber has quite rough accuracy? to describe back-mixing in reactor, since it only functions in integers of n . Replacing factorial $(n - 1)!$ into function of $\Gamma(n)$ allows the function to work with non-integer n values (Toson, Doshi & Jajcevic, 2019). $\Gamma(n)$ is an infinite integral equation that extends factorial to any positive value: (Britannica, 2022)

$$\Gamma(n) = \int_0^{\infty} x^{n-1} * e^{-x} dx \quad (9)$$

Equation allows fitting model with values of $n < 1$, which can be used to fit models describing a bypassing flow in the reactor (Fig 10) (Toson, Doshi & Jajcevic, 2019). Equation for model where factorial is replaced with $\Gamma(n)$:

$$E(t) = \frac{t^{n-1}}{\Gamma(n)} \left(\frac{n}{\tau}\right)^n \exp\left(-\frac{t n}{\tau}\right) \quad (10)$$

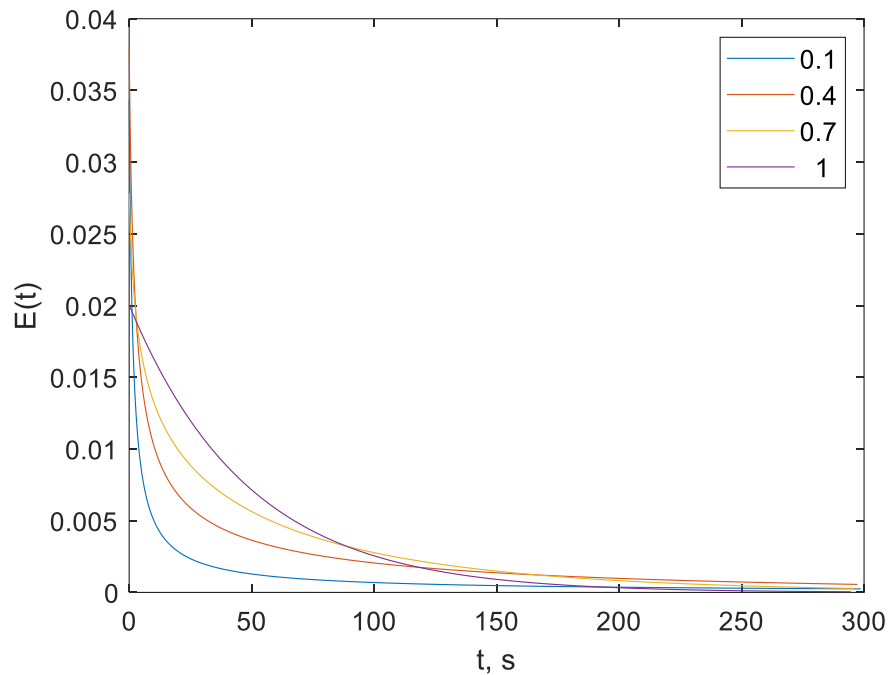


Figure 9. Example of different amounts of bypassing in CSTR exit time curve

In equation (7) the degree of bypassing alters the mean residence time, but equation (10) can be used to define bypassing without changing it, since the initial peak increases accordingly with degree of bypass. Model where $n < 1$ might seem unrealistic, but it describes conditions where reactor designs such as inlet and outlet positioning allows material to exit in a shorter time than intended (Fig 10) (Toson, Doshi & Jajcevic, 2019).

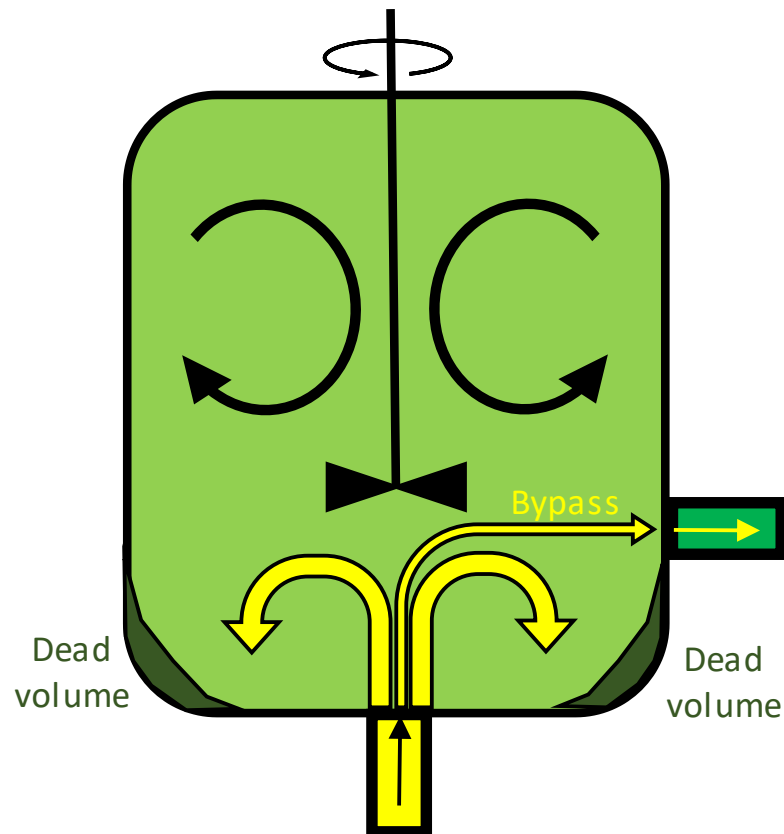


Figure 10. Visualization of dead volume and bypassing in a CSTR

Fraction of bypassing material is explained in (Fig 11), as when n becomes smaller the bypassing factor grows exponentially. Three plots displayed are 1, 5 and 10% of the mean residence time for a reactor. When $n \rightarrow 0$ curve becomes a vertical Dirac delta pulse as all material bypasses the reactor. Dirac delta pulse is a vertical line with area of 1 and width of 0 (Toson, Doshi & Jajcevic, 2019).

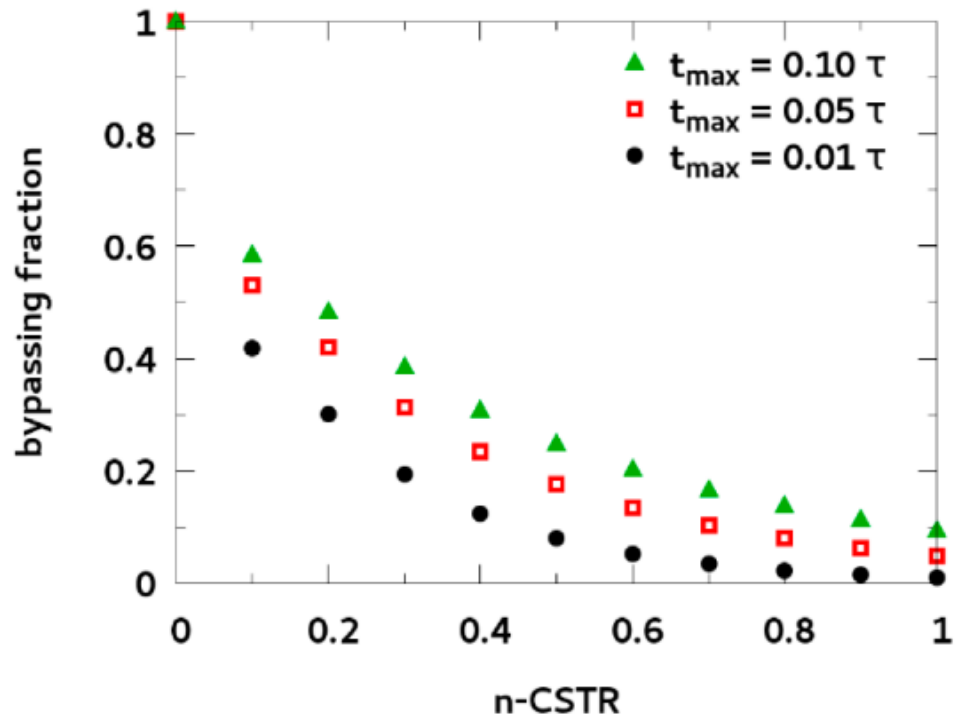


Figure 11. Bypass fraction over different fractions of n (Source: (Toson, Doshi & Jajcevic, 2019))

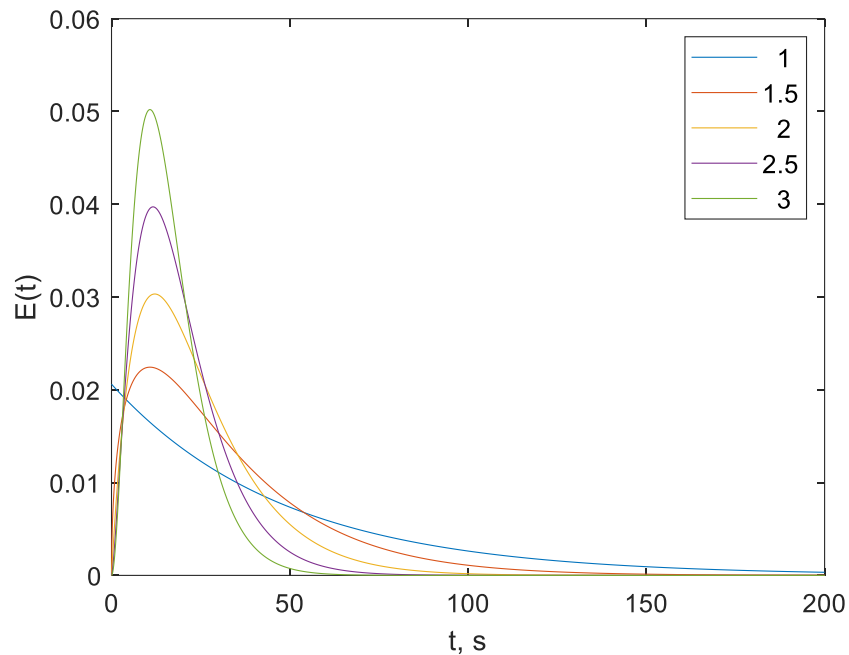


Figure 12. Example of fractional CSTR cascades depicting back mixing

Results in (Fig 12) are similar than in (Fig 6), but as can be seen from the figure an increase of 0.5 for n notably changes the curve. This equation allows fine tuning to estimate more accurate models for the experimental data.

3.3 n amount of CSTRs in series with recycle:

Single parameter models may not provide best possible fit to real reactor systems, so therefore flow models with multiple parameters have been developed to provide best possible understanding of flow mechanics in a system (Fu et al., 1971).

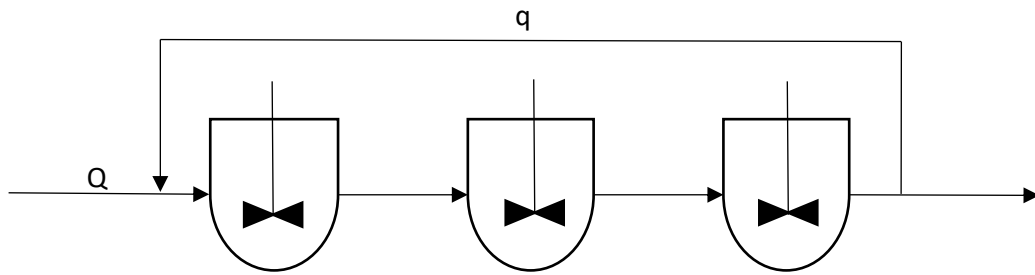


Figure 13. System of CSTR cascade with recirculation stream

$$E(t) = \frac{1}{R} \sum_{m=1}^{\infty} \left(\frac{R}{1+R} \right)^m \frac{1}{T_n^{mn}} \frac{t^{mn-1}}{(mn-1)!} \exp\left(-\frac{t}{T_n}\right) \quad (11)$$

$$T_n = \frac{V_n}{Q(1+R)} \quad (12)$$

where	R	recycle ratio, Q/q
	q	recycle stream volume flow, L/h
	T_n	time constant
	m	number of convolutions, an integer

When $n = 1$, altering recycle stream does not change RTD for a single stirred tank, as ideal CSTR is independent of R (Fu et al., 1971). When n value is greatly increased, oscillation begins to occur in the exit time curves.

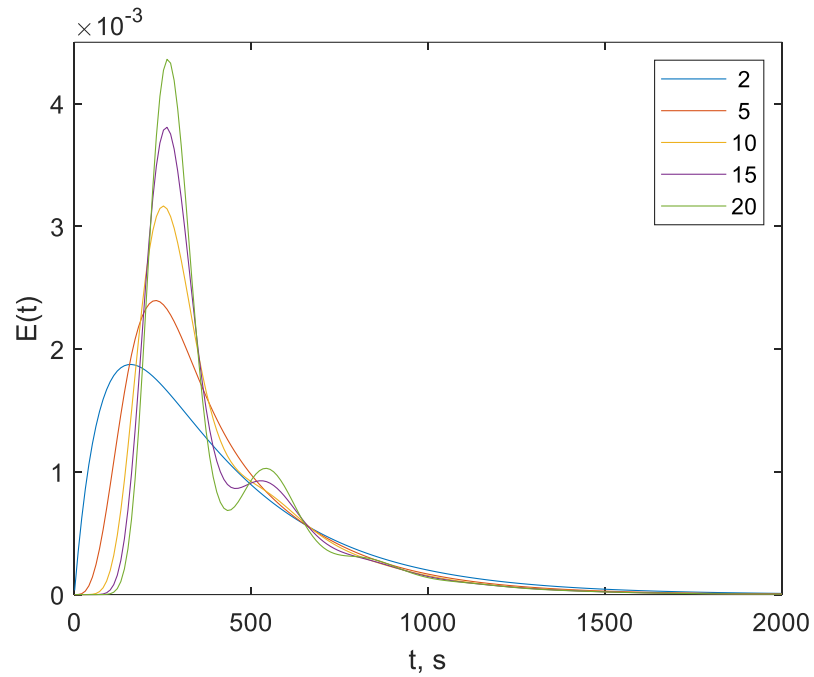


Figure 14. Exit time curves for different lengths of CSTR cascades, where recycle ratio $R = 1$.

3.4 Non-integer n with recycle stream

Combining the equations (9) and (11) results into equation that can be used to fine tune fraction of back mixing with recycle stream present. Using values of $n < 1$ model describes conditions when bypassing occurs in the presence of recycle stream (Toson, Doshi & Jajcevic, 2019).

$$E(t) = \frac{1}{R} \sum_{m=1}^{\infty} \left(\frac{R}{1+R} \right)^m \frac{1}{T_n^{mn}} \frac{t^{mn-1}}{\Gamma(m * n)} \exp\left(-\frac{t}{T_n}\right) \quad (13)$$

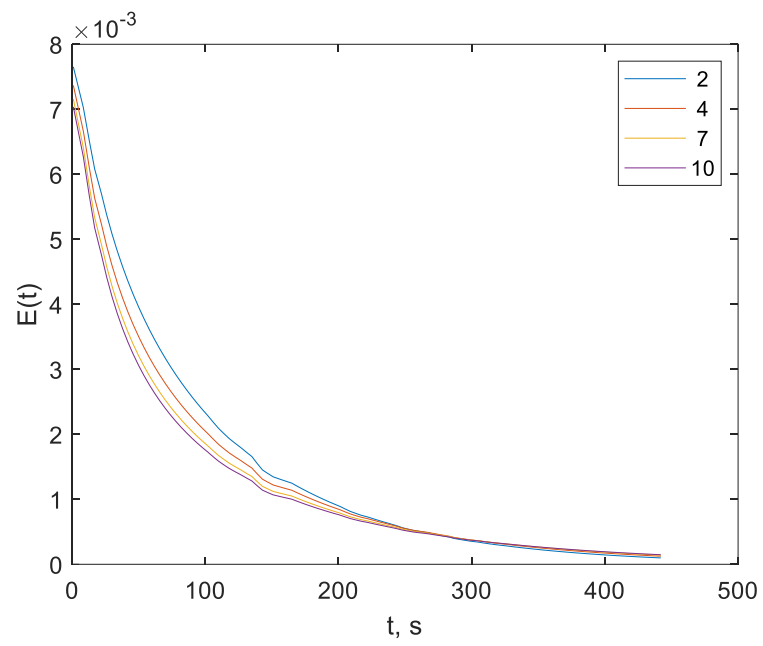


Figure 15. CSTR with a bypassing flow and varying recycle streams q

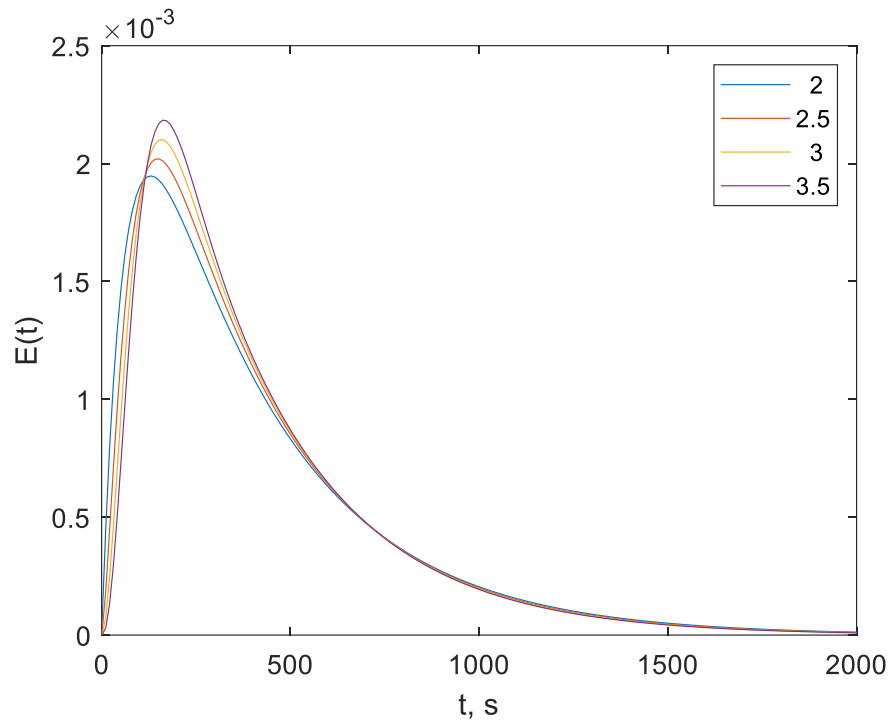


Figure 16. Different lengths of CSTR cascade with recycle ratio $R = 1$.

This two-parameter model contains a lot of flexibility at fitting a model but brings a heavy computational load in MATLAB because of the gamma-function and recycle stream integration.

4 Experimental setup

Residence distribution time experiments were conducted in MSU-0.5 Laboratory Mixer-Settler Unit by Metallextraktion AB (Fig 17). Mixer side has a volume of 0.12 dm³ CSTR and it is equipped with variable speed motor that can be adjusted to different mixing speeds (MEAB, 2019). Settler side is a 0.46 dm³ open tank and can be depicted as a PFR in modelling. It has a picket fence right after the mixer to enable an even flow distribution from mixture to the settler, and a recycle option to direct heavy phase back to the mixer. Back of the settler contains the heavy phase removal screw which has a hole where heavy phase flows exits the system (MEAB, 2019).

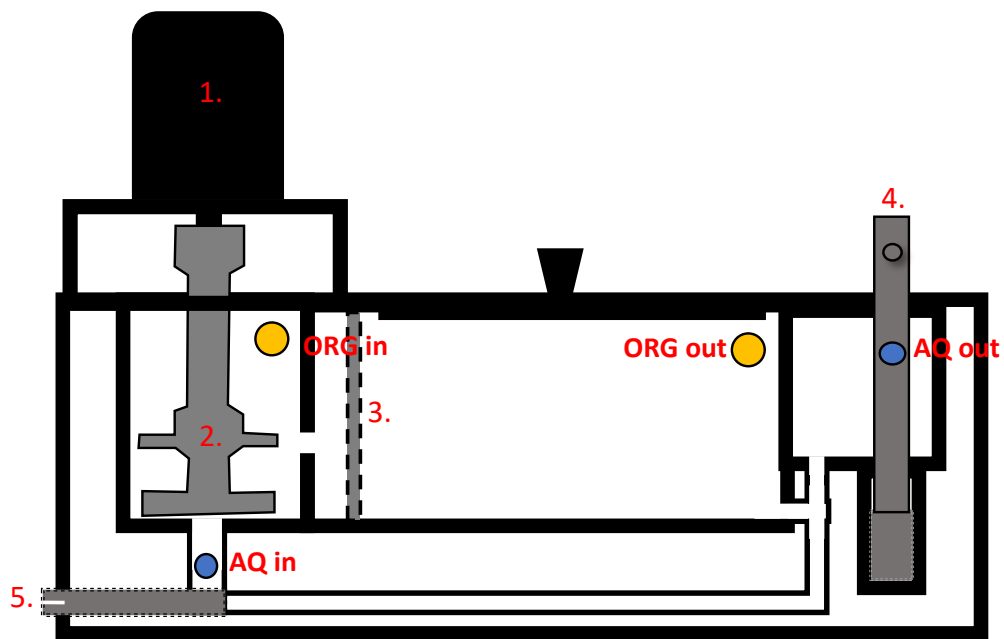


Figure 17. Side view of the used MEAB MSU 0,5 unit

1. Mixer motor
2. Mixer impeller
3. Picketfence

4. Height adjustable screw for heavy phase removal
5. Recycle stream adjusting screw

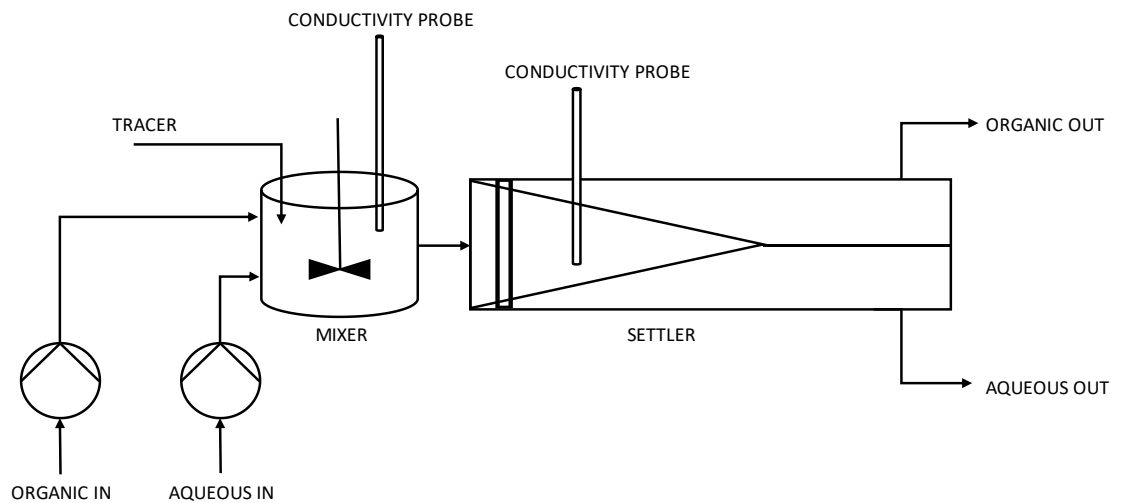


Figure 18. Process layout of the experimental setup

(Fig 18) displays process layout of the system used. Mixer side conductivity probe is submerged in emulsion of both phases, and settler side probe was submerged below organic phase into aqueous phase.

Choice for placement of conductivity probes is explained later in experimental part. Mixer contains a slit which allows the mixed solution to flow into the settler. Slit is angled according to the rotation of the impeller, depicted in (Fig 19):

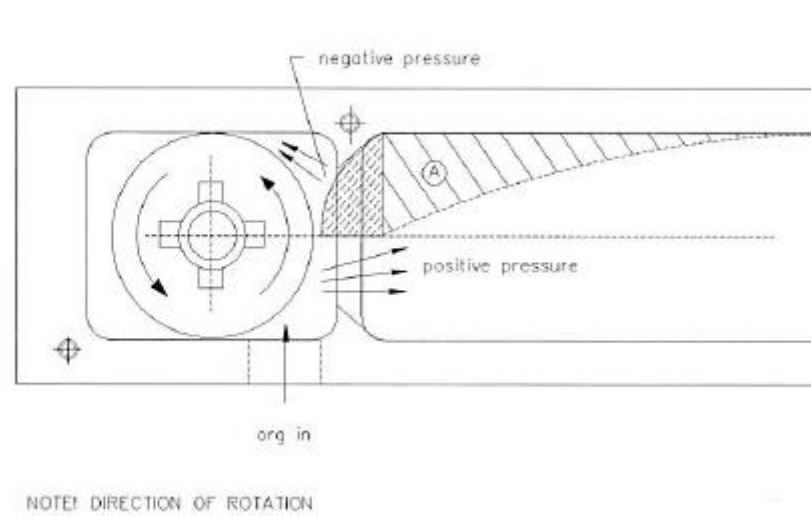


Figure 19. Top view of the mixer outlet flow to settler (Source: MEAB, 2019)

The letter A describes a stagnant volume that forms to settler at opposite side of the slit due to the uncentered flow.

4.1 Choosing the tracer for RTD experiments

Simplified method to form an exit time curve requires a conductivity curve that extends in linear manner. Chloride salts are a popular choice for conductivity tracer material for their high conductivity even in tiny concentrations and their inert characteristics, since it is essential that no mass transfer occurs between aqueous and organic phase when measuring aqueous phase RTD in a two-phase liquid-liquid system. (Alizadeh, Hosseinzadeh, 2013).

KCl was the tracer chosen for its linear relation in conductivity over concentration, which other common salts do not necessarily possess (Rumble, 2022a). (Fig 20) shows how concentration affects conductivity of KCl and other commonly used salts, values are standards obtained from CRC Handbook of Chemistry and Physics Online:

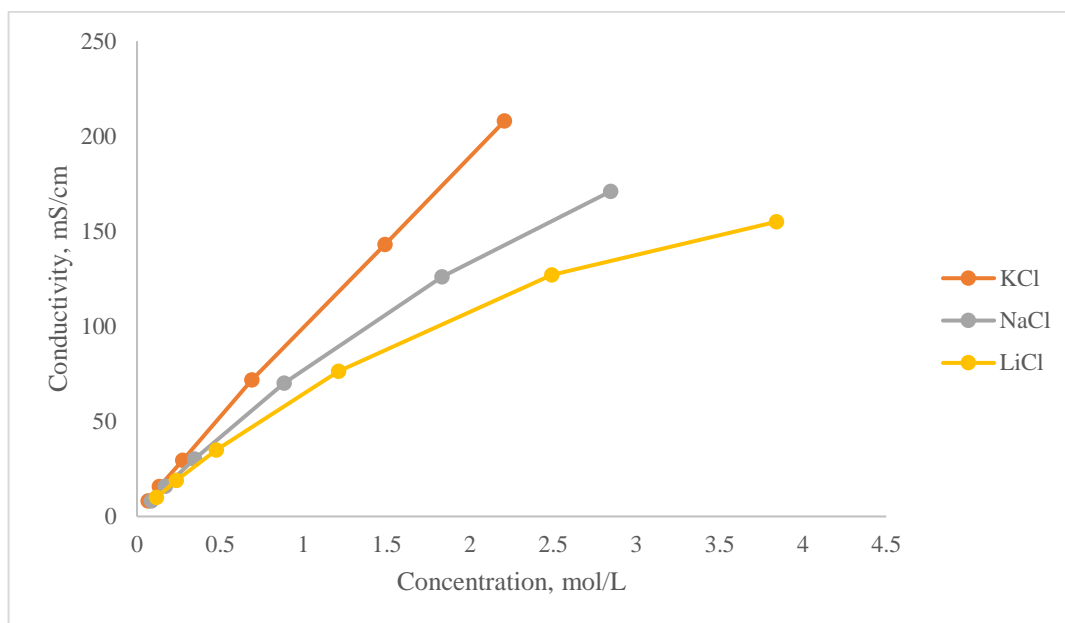


Figure 20. Concentration to conductivity correlations for different common salts (Rumble, 2022).

For 2-phase tests, both aqueous phase and organic phase RTD are of interest, and separate tests and measurement methods need to be implemented. In previous studies, aqueous phase residence time distribution has been successfully measured using conductivity, so KCl solution was the tracer of choice for aqueous phase RTD in 2-phase system (Aminian, Bazin & Hodouin, 1998).

Organic phase residence time is difficult to measure through conductivity since aqueous solutions such as KCl and organic solvents do not blend together. Widely used method for measurement for organic phase RTD is radiotracer methods that use radioactive materials such as Sodium-24, Iodine-131 and Xenon-133 (IAEA, 2008). Unfortunately, in this research radiotracers were not available so other methods had to be used.

Method chosen was to use another organic material as the tracer and measure the concentration change over time offline by taking samples from the system and analyzing them. 0.8 M DEHPA was chosen as the tracer since it has different molecule structure and functional groups than solvent used Exxsol, and DEHPA content should be measurable from Exxsol through analytical methods.

4.2 Conductivity data logger

Consort C3060 multiparameter analyzer was used to measure and log the conductivity readings from the mixer-settler (Fig 21). Consort 3060 has ports for two conductivity probes, so two probes were used throughout the experiments to gain additional data.

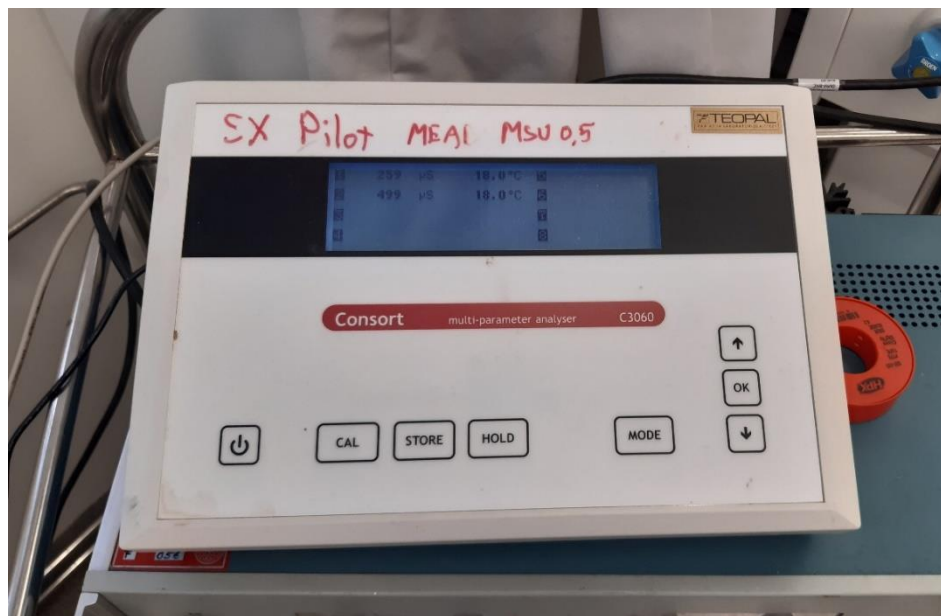


Figure 21. Consort C3060 multiparameter analyzer

KCl solution with concentration of 0.01 mol/L was prepared for calibration of the conductivity probes, and they were calibrated daily before the experimentation. Accuracy of the conductivity measurements was not required to be highly accurate, since data would be normalized before forming exit time curve, but probes needed to be calibrated to the same reading so that both probes react similarly to same concentration of KCl.

Conductivity data over time was collected using Consort datalogger software stable and unpacked with MATLAB script to readable form. Time interval for each reading was 2 seconds as long as conductivity reading was stable enough.

4.3 Feed pumps used

Delta OptoDrive diaphragm (Fig 22) pump was used to feed deionized water into the bottom of the mixer. It was used in ranges between 3 – 10 L/h and continuous flow pump was used in 1 – 2 L/h range. This was due to the pulsating nature of diaphragm pump, which is more severe in small volume flows and could affect the results.



Figure 22. Diaphragm pump used to feed deionized water to the mixer

Total experiment time was measured and both phase outlets were directed into containers, and their masses weighed after experiments. This was necessary since volume flow reading given by the pump was often inaccurate, and precise volume flow is needed to calculate exit time curve.

4.4 Power unit for mixer adjustment

Mixing speed was adjusted just below where air bubbles start to form in the mixer (MEAB, 2019b). This was done by using an AC to DC converter (Fig 23) with adjustable current, and optimal mixing was found with voltage of 7.0 V and electric current of 0.1 A for 1-phase experiments.



Figure 23. Power supply used to operate mixer

In 2-phase experiments, voltage for mixing was adjusted to 8.5 volts so that phase border visually completely disappears in the mixer but phases could still separate without issues at settler side.

4.5 Linearity of conductivity curve

RTD experiments were conducted by using highly conductive KCl solution as a tracer, that has a relatively high conductivity even in tiny concentrations. Conductivity was measured in different concentrations to confirm that conductivity increases in linear fashion at the smaller concentrations where the experiments revolve around. Conductivity calibration curve was done using concentrations between 0.25 mmol/L and 1 mol/L and (Fig 24) displays the results:

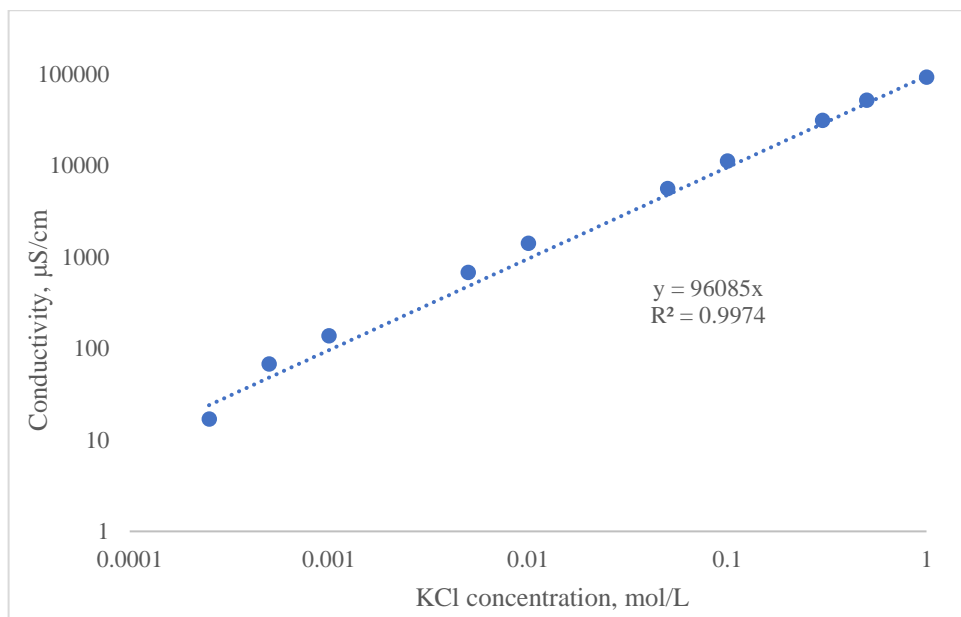


Figure 24. Measured conductivities in different KCl concentrations

Conductivity at 1 mol/L is 93 200 μS/cm and beneath that the concentration curve follows a linear model. This calibration curve also allows to estimate concentrations occurring in the mixer-settler.

4.6 Density measurement of the phases used

Density for both aqueous and organic solution was measured to further increase accuracy of volume flow measurement. Density meter used was DDM 2911 Automatic Density meter from Rudolph Research Analytical.

Table 1. Density measurements for both phases

Purified water T = 20 °C	Exxsol D80 T = 20 °C
0.994 g/cm ³	0.8096 g/cm ³

5 Experimental methods

Metallextraktion AB's manual for MEAB MSU-0.5 mixer-settler unit (Fig 25) describes mixer volume to be 0.12 dm^3 however it was discovered that for 1-phase system, volume of the mixer and settler depends on the height of outlet screw shown on (Fig 17). Outlet screw was set so that liquid level settles barely below organic outlet, as it would be in a two-phase experiment.

For two phase experiments outlet screw was adjusted so that phase border sets at the height of the outlet slit according to instructions. Volumes of mixer and settler in two phase experiments are constant, since surface of the liquid is defined by outlet of organic material (Fig 17).

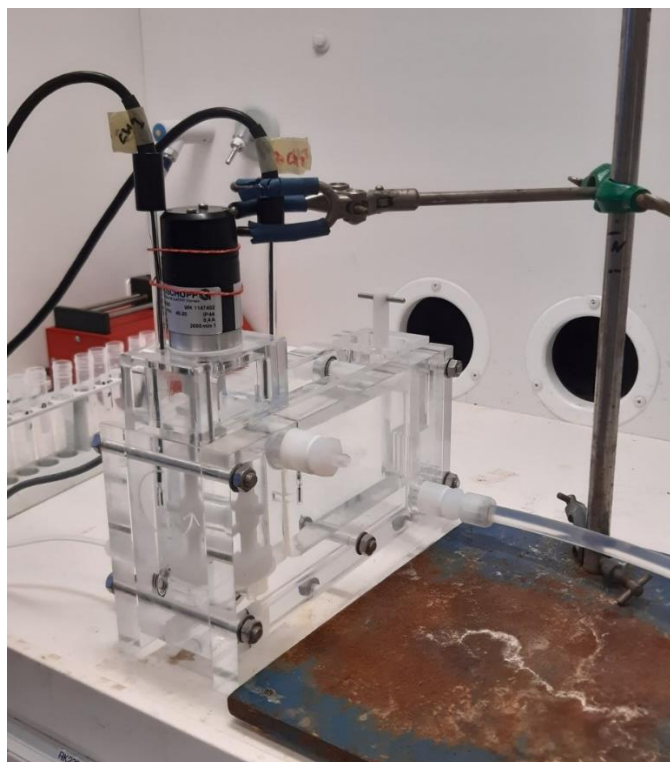


Figure 25. Experimental setup showing MEAB mixer-settler unit and the conductivity probes.

5.1 Conducting tracer test

Pulse tracer test usually provides more information than step input test, and compartment models depicted by Levenspiel can be used to describe possible meanings of different type of exit time curves. Both Aminian and Alizadeh also use pulse test in their research of mixer-settler systems, so it was the primary method chosen for the RTD tests (Aminian, Bazin & Hodouin, 1998) (Alizadeh, Hosseinzadeh, 2013).

Pulse experiments were done by using 3 mol/L KCl solution and injecting 1 mL of it from top of the mixer displayed in (Fig 26).

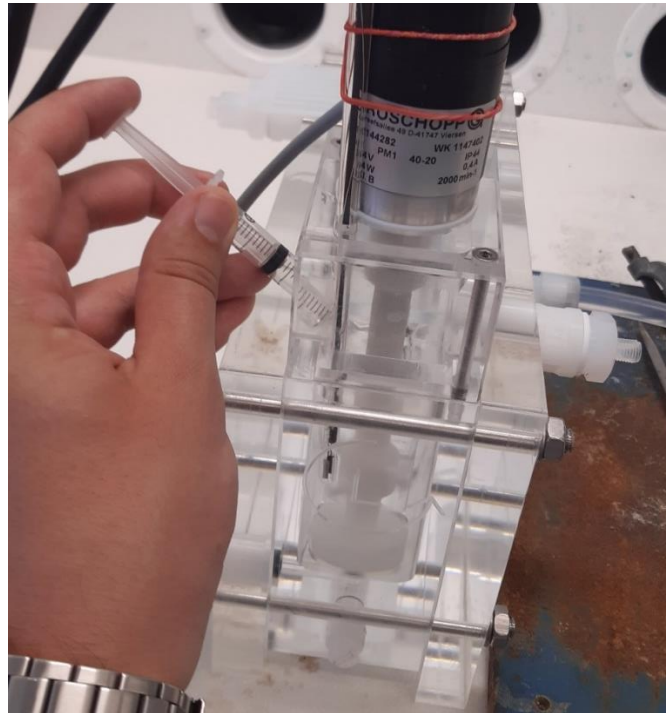


Figure 26. Injection of tracer to the mixer

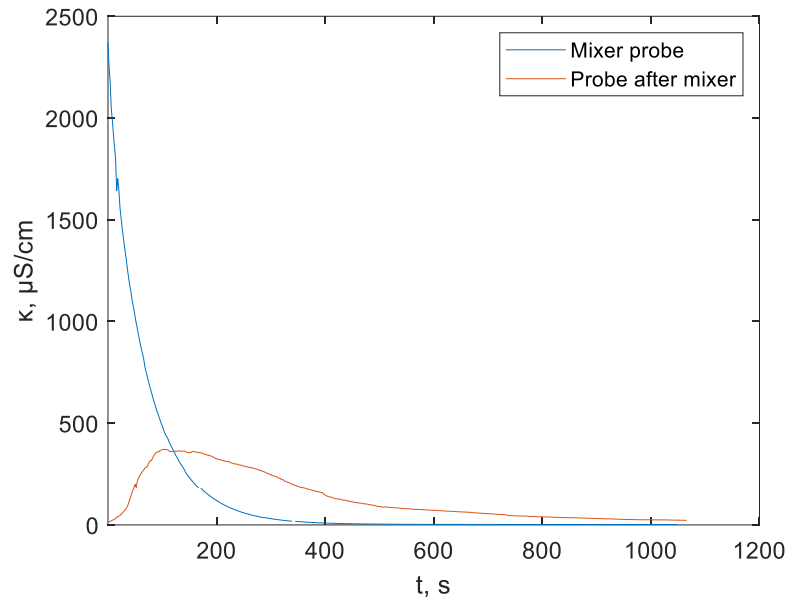


Figure 27. Conductivity curves of mixer and settler through time in a 1-phase system

In the conducted experiments, even though mixer side conductivity had dropped to base water level, settler side probe continued to measure readings of conductivity and can be seen from (Fig 27). This is due to hydrodynamics inside settler side meaning that for example stagnant region or recycling flow causes tracer to not flow linearly out of the system.

Observation was made cleaning the system when settler side still contained liquid some material and mixer was empty, liquid was dripping from the aqueous phase inlet. This means that the recycle rate adjustment screw (Fig 17) was not 100% watertight, and some degree of recycling might take place. However, the amount of recycling was not severe and deemed impossible to measure so it was not accounted in the model fitting.

5.2 Placement of the conductivity probes

MEAB mixer-settler used did not have an obvious place to measure residence time distribution for the mixer system, since mixer and settler are integrated into one unit. Placement of the conductivity probes was studied to find measurements that would provide high quality residence time distributions.

Normally measurement probe is placed at the outlet of the reactor to track concentration changes over time (Datta, Bhunia & Gupta, 2021). In this case, probe placement is not that simple since mixer outlet to settler side is only about 1x2 cm slit and placing a probe directly behind it could change hydrodynamics of the system.

Placing settler side probe just behind the mixer was initially tested to obtain a model for mixer performance, but difficulties were faced in finding a model to describe the data. Probe positioning was investigated, and first test was to check does probe height have effect in settler side (Fig 28). Normal level was considered as the level where probe is submerged to the height of outlet slit so tests were made to measure conductivity higher and lower that height.

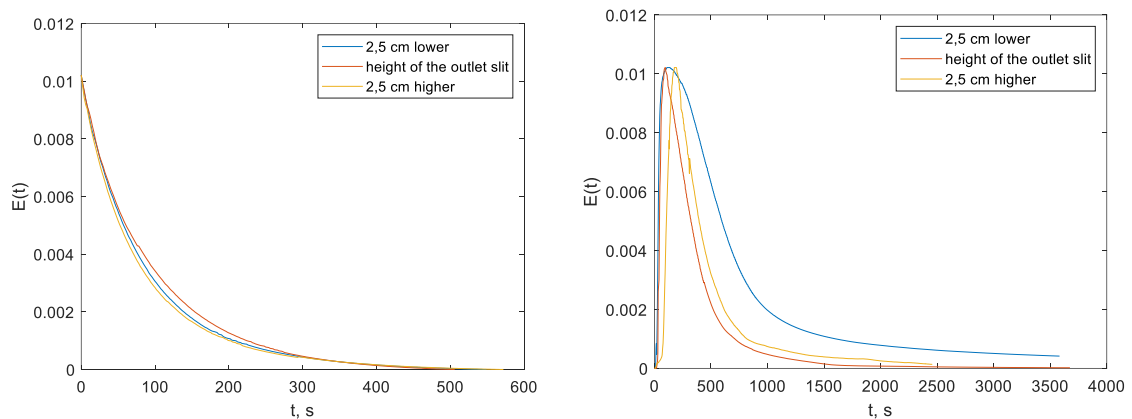


Figure 28. Raw data describing the effect of settler probe height to mixer and settler data, mixer data is on the left and settler data on the right

Probe height was found to have minimal to no effect to mixer side performance, but settler side curve changed with the height of probe. Lower probe placement resulted into a much longer tail in the conductivity curve, which differed a lot from the higher probe placements. This was a result from a stagnant region or constant back mixing (Fogler, 2006).

This result raised questions about reliability of calculating exit time curve from settler side. Since small change to the height of the probe completely changed the results, accuracy of measurements from settler side become questionable. Second test was done examining probes distance to mixer at settler side (Fig 29).

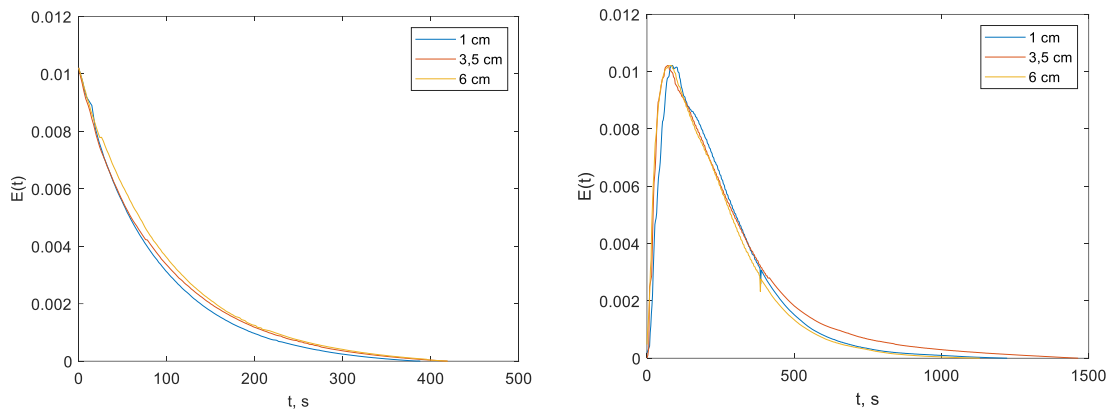


Figure 29. Raw data describing the effect of settler probe distance to mixer, mixer data is on the left and settler data on the right

Mixer data exit time curves had very minor deviances from each other, so conclusion can be made that mixer performance is not affected by probe distance.

Settler data has been adjusted so that every curve begins at 0 s. Even the raw conductivity data curves in settler are very similar, so probe distance does not matter in settler data. Mixer side exit time curve has an area of ~ 1 but area of settler side $E(t)$ is over 3, meaning that settler side flow mechanics interfere with the measurement even at 1 cm distance to the outlet gap. (Fig 19) displays the stagnant region at the opposite side of the outlet slit and possibly it traps some tracer and then slowly seeps it out, resulting into much longer residence time distributions than in mixer side.

Final probe placement tests were done by placing probe right behind mixer outlet gap and studying the resulting exit time curves, to analyze does it affect to the performance of mixer (Fig 30):

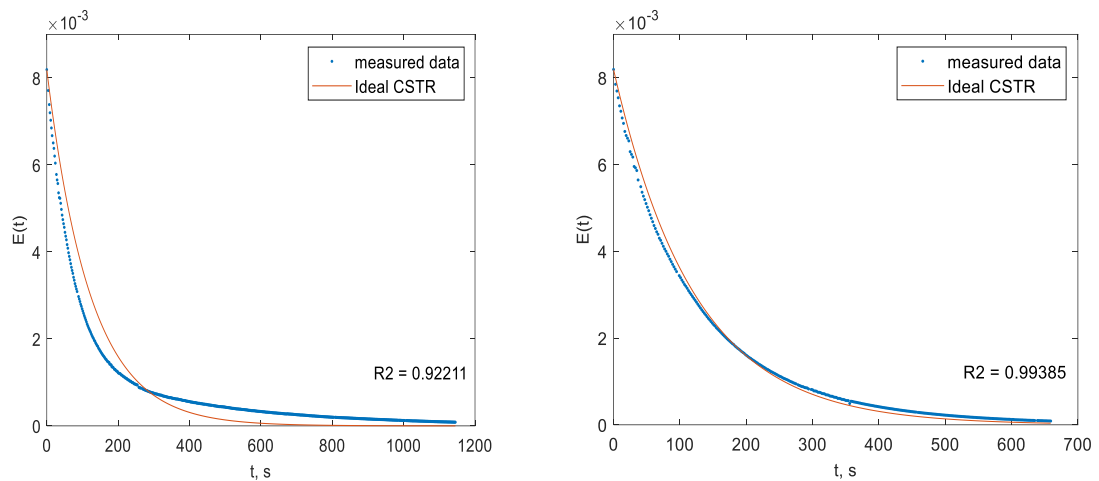


Figure 30. Comparison of mixer performance when changing position of the probe, left figure displays probe directly behind the outlet and right figure with a distance of 2.5 cm

Exit time curves confirm that now mixer performance is hindered when probe is placed right behind the outlet shown in the left figure, and conclusion is that RTD measurement cannot be done reliably from settler side. Settler hydrodynamics interfere with the probe, and directly behind the mixer outlet slit it interferes with performance of the mixer.

Measurement directly from the mixer is a more uncommon practice but it has been done by Onyemelukwe et al. and Hu et al. conducted experiments where measurement directly from the mixer was used as a method to measure imperfect signal for stirred tank reactor cascade (Onyemelukwe et al., 2018). Hu et al. conducted a CSTR-cascade pulse experiment, where tracer was injected into the first CSTR and performance of each CSTR was analyzed by using RTD (Hu et al., 2020).

Since measurements could not be done from the settler side, conductivity measurements for mixer residence time distribution were measured directly from mixer for both 1- and 2-phase experiments.

6 Two phase RTD experiments

Next experiment is to operate mixer-settler system with the presence of both organic and aqueous phase, as it would operate in real life conditions. Aqueous phase RTD data is measured through conductivity measurements similarly than in single phase experiments by using KCl pulse as a tracer (Rajavathsavai, 2012). In organic phase experiments, a DEHPA pulse is injected into the mixer and samples are taken from the mixer. Samples are then analyzed to determine reduction of tracer concentration over time.

6.1 Aqueous phase RTD

Successful RTD measurements from aqueous phase require that no mass transfer occurs between aqueous and organic phase (Aminian, Bazin & Hodouin, 1998). This was determined by mixing a 0.1 M KCl solution and Exxsol D80 in a separation funnel and collecting the organic phase exposed to KCl solution. Conductivity was measured and compared to unused Exxsol. Both showed conductivities $>1 \mu\text{S}/\text{cm}$, so it was concluded that there is no ionic mass transfer between aqueous and organic phase.

Issue was faced at the organic phase RTD experiments when droplets of organic phase would accumulate inside the conductivity probe even though the presence of heavy mixing and phases visually completely dispersing. Probe height and rotation were adjusted but this seemed to have no effect, but slight increasement to mixing power provided slightly more reliable results. Some of the experiments failed completely as the mixer probe would trap droplets of organic phase and conductivity curve would plummet to $1\text{-}2 \mu\text{S}/\text{cm}$ and remain there for a period of time, and suddenly start measuring normally again as the organic material exits the probe (Fig 31). Especially data in the first minutes is crucial, so only results were used where the conductivity curve is intact and showed no signs of interference by organic phase.

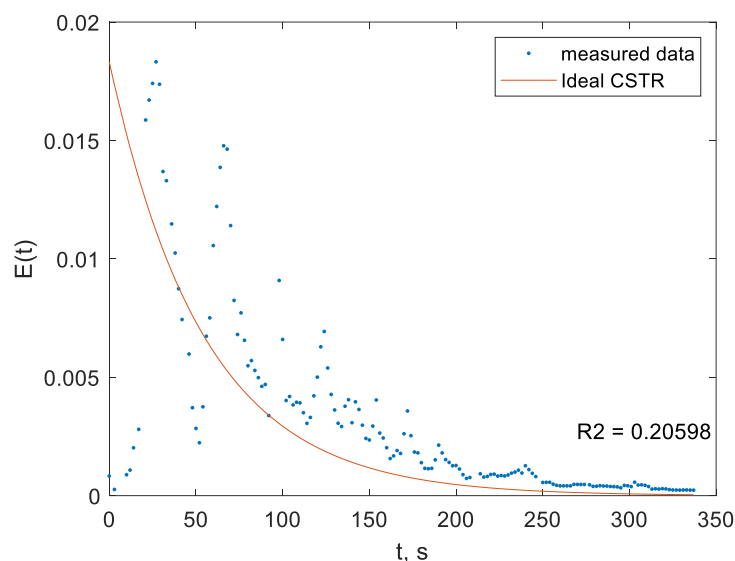


Figure 31. Failed conductivity measurement.

6.2 Organic phase RTD

Organic RTD tests were conducted by injecting a tracer of organic liquid. Since radiotracers were out of question, no online measurement solution was found to measure RTD. Measurement was done offline by taking samples with a timer that was used to mark the time sample was taken. Problem is the volume required for samples, since mixer volume is only 0.136 dm^3 and for example by taking 5 mL of sample every 10 seconds would mean that after 4 min the total volume of samples would be same as the mixer volume. Therefore, sample size needed to be small and time interval relatively long so most of the tracer is not removed through samples.

Decision for the sampling method was to take 1 mL samples in 15 s interval, and after 3.5 min samples were taken every 30 seconds. This was done because the most significant concentration change occurs in the first minutes and gradually slows down towards the end.

6.3 Analysis method for organic RTD

Analysis method for organic tracer was carefully thought, since each sample was 1 mL and contained ~500 μL of organic sample so only 1-2 analyzes was possible to conduct.

Titration was tried initially for its speed and simplicity to measure the DEHPA concentrations from the Exxsol. For each sample 200 μL of organic phase was removed with pipette and diluted in isopropanol alcohol, and titration was done using NaOH solution. Various molarities of NaOH was tried in titration to find the equilibrium point with concentrations ranging from 0.1 to 0.0001 mol/L, but results were either nonobtainable or inconsistent so it was determined that detection range of titration was not sufficient.

Gas chromatography was next plausible method and samples were prepared by diluting 0.2 mL of organic sample to 0.8 mL of pure Exxsol. Tracer of choice DEHPA is known to have its GC spike at different time than Exxsol so GC should be able to recognize them accurately from each other. However, the DEHPA concentrations in the samples proved to be too low to be recognized and measured by GC.

7 Results and discussion

Conductivity measurement was successful for finding RTD in 1-phase experiments and for aqueous phase in 2-phase experiments. Resulting conductivity readings increased almost instantly to maximum reading similarly than in measurements conducted by Choi et al., where results also showed close to ideal CSTR behavior (Choi et al., 2004). Conclusion of the organic phase residence time distribution experiment was that DEHPA concentrations are too low for GC measurement, so this analyzing method is not suitable to measure RTD for organic phase.

7.1 Results from 1-phase experiments

Pulse tracer tests were done from 1 to 10 L/h to investigate performance of the reactor when only one phase is present (Table 2).

Table 2. Different volume flows compared to ideal CSTR model

Q, L/h	R2	HRT, s
1.18	0.6852	366.1017
2.23	0.8607	193.722
3.19	0.986	135.4232
4.01	0.9938	107.7307
4.89	0.9925	88.34356
5.9	0.9924	73.22034
6.71	0.9972	64.38152
7.78	0.9979	55.52699
8.96	0.9952	48.21429
9.76	0.9998	44.2623

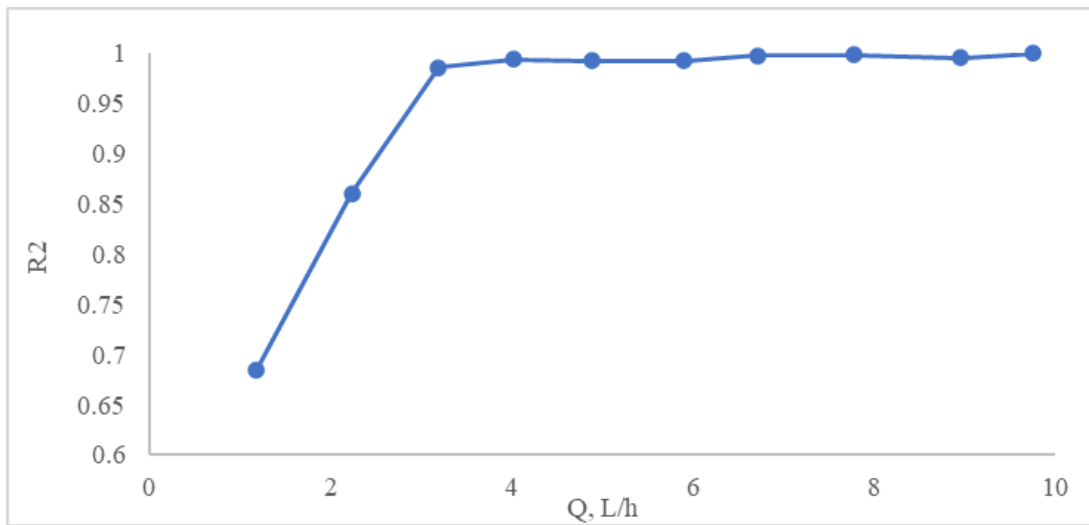


Figure 32. Different volume flow results compared to ideal model for one phase system

Feed volume flows lower than 3 L/h were found to have massively inferior performance. Initially it was thought that reason was the pulsating flow of diaphragm pump, which was severe at the lower feed flow but using continuous flow the results were similar. When 1-5 L/h pulse measurements are fitted into same figure (Fig 33), the 1.18 and 2.23 L/h experiments clearly stand out from the rest.

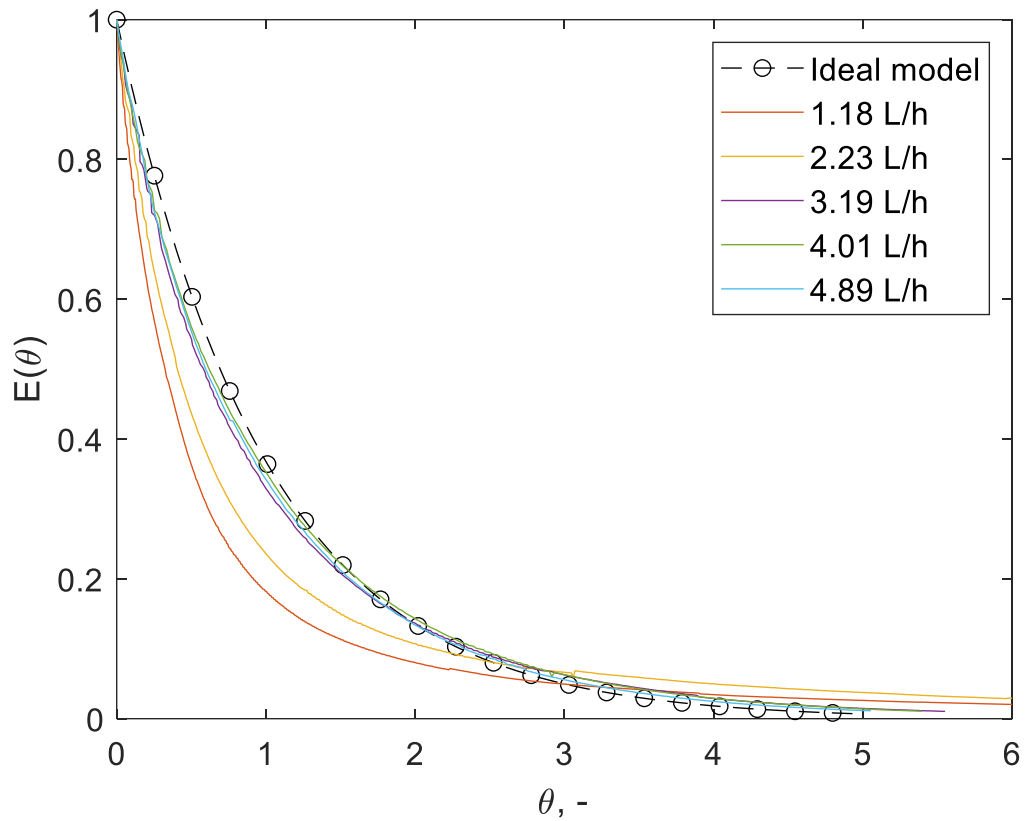


Figure 33. Volume flows of 1 – 5 L/h compared to ideal model

Exit time curves measured show a threshold at ~ 3 L/h, where volume flows 3 or higher closely followed ideal model, all had R^2 values over 0.98 and 10 L/h was the peak at $R^2 = 0.9998$. When 6 – 10 L/h are compared, the differences between them are minimal as they follow the ideal model even better (Fig 34).

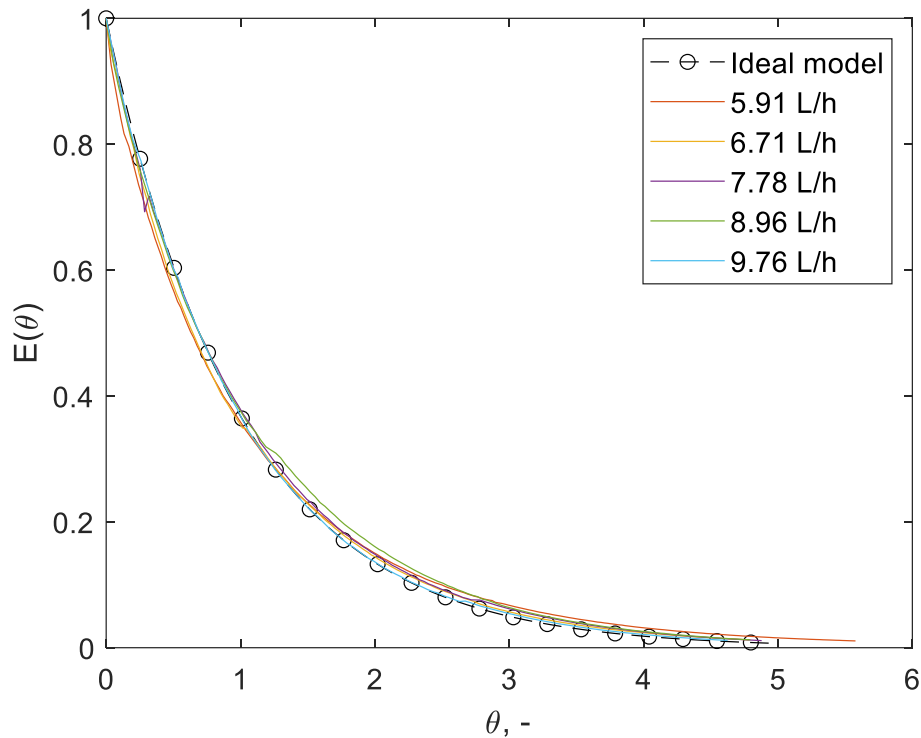


Figure 34. Pulse experiment data from 6 - 10 L/h

Other research regarding performance of a single CSTR RTD suggested that reactor performance moves from dispersion towards ideal mixing at higher volume flows (Rajavathsavai, 2012). Other experiments report similarly that higher volume flow leads to turbulence and better mixing, but could also change the mixer volume (Gordon et al., 2014). Findings and this report support these previous observations, but the degree of these phenomenons require further research.

7.2 Flow model fitted to 1-phase data

Bypassing was successfully used to describe flow model for 1-phase experiment results. Fraction of bypassing became smaller as the volume flow increased, and bypassing grew significantly at below 3 L/h.

1.18 L/h data was fitted with a model where $n = 0.25$ and recycle flow is 2.25 L/h. When this data is fitted with (Fig 11) describing degree of bypassing, it shows that 40% of the tracer exits the mixer after 0.1τ which equals to 22 s (Toson, Doshi & Jajcevic, 2019).

Exit time curve for 2.23 L/h greatly differed from ideal model, and it was fitted with $n = 0.6$ describing large fraction of bypassing taking place (Fig 35).

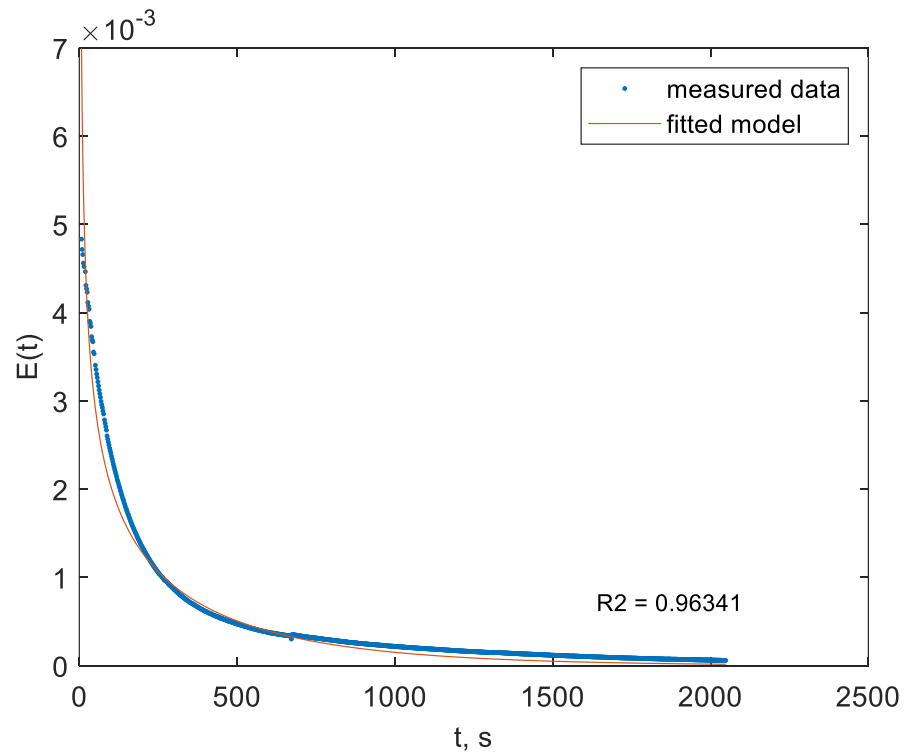


Figure 35. Heavy bypassing fitted to 2.23 L/h data where HRT = 194 s

Volume flows of 3 – 10 L/h were nearly ideal and had only minor difference to each other, and they were all fitted with nearly the same amount of bypassing (Fig 36).

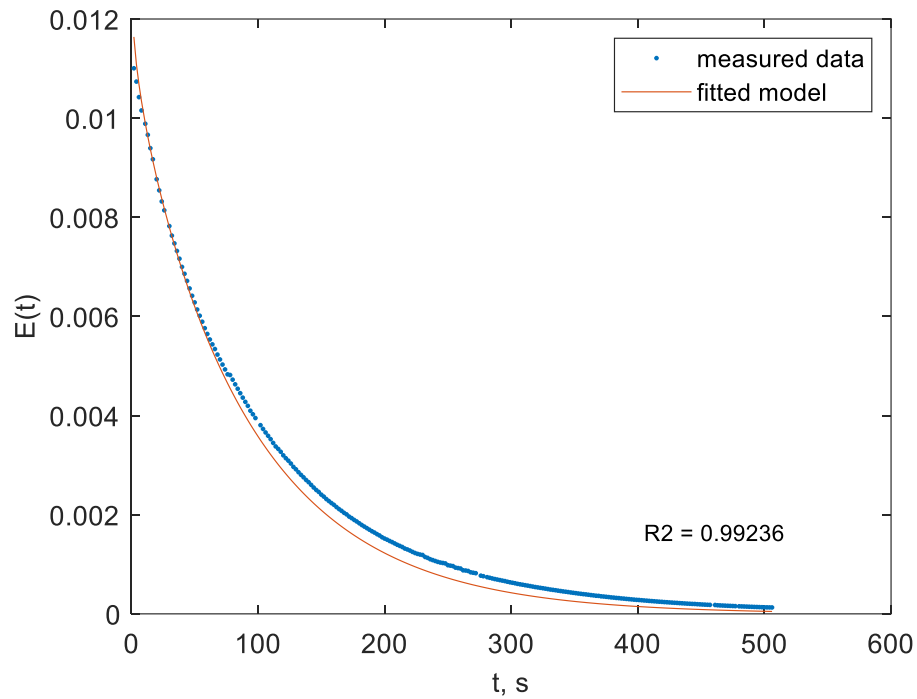


Figure 36. Minor bypassing of $n = 0.93$ fitted to 4.89 L/h data

Best fitting model was found to be bypass flow which is formed by fitting model with n values between 0 and 1. Lowest volume flow used 1.18 L/h was found to be an exception, that followed a model with both bypassing and recycle stream. Results indicate that bypass decreases towards higher volume flows, and mixer approaches ideal CSTR model according to residence time distribution (Fig 37).

Table 3. Fitted models and their R2 values

Q, L/h	n	R2
1.18	0.25, q = 2.5 L/h	0.986
2.23	0.6	0.983
3.19	0.89	0.9954
4.01	0.92	0.9981
4.89	0.93	0.9975
5.9	0.94	0.9968
6.71	0.96	0.999
7.78	0.98	0.9978
8.96	0.97	0.9955
9.76	1	0.9998

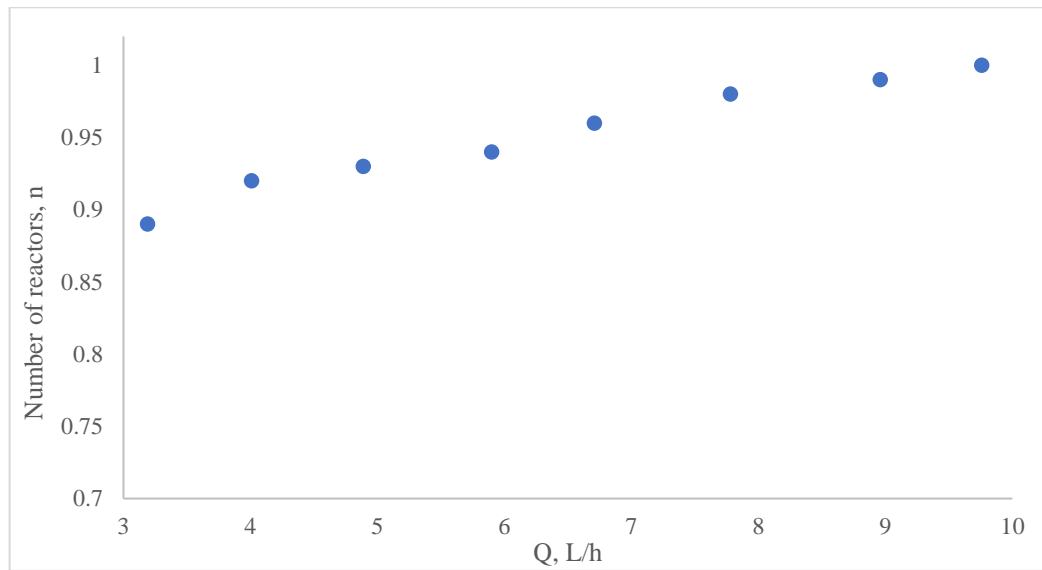


Figure 37. Bypassing models fitted to different volume flows

7.3 Results from 2-phase RTD measurements

Introducing both phases to mixer-settler system provided contradicting results to the previous one phase experiments. (Fig 38) below showed a curve area of 139% indicating that back mixing occurs at this feed rate.

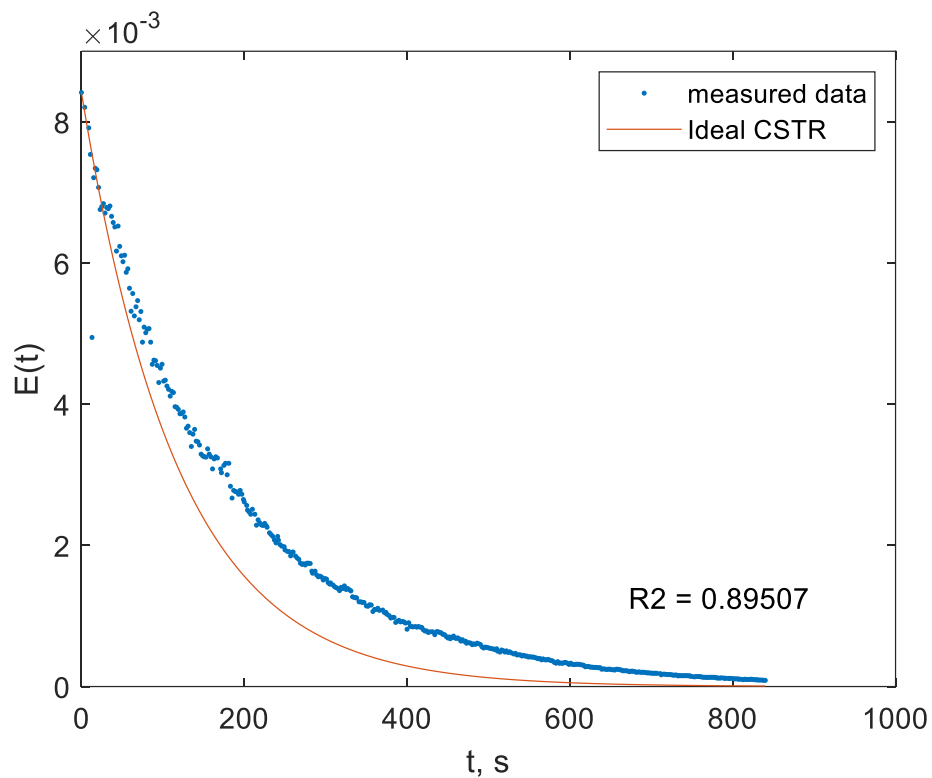


Figure 38. Exit time curve from 2-phase experiment for aqueous phase where volume flow was 4.01 L/h and HRT = 105 s

This is caused due to back mixing inside the mixer, and tracer exits slower from the system than in an ideal model (Pinto et al., 2004). Higher volume flows were experimented to find out how exit time curve behaves in larger feed rates, and following results were obtained (Fig 39):

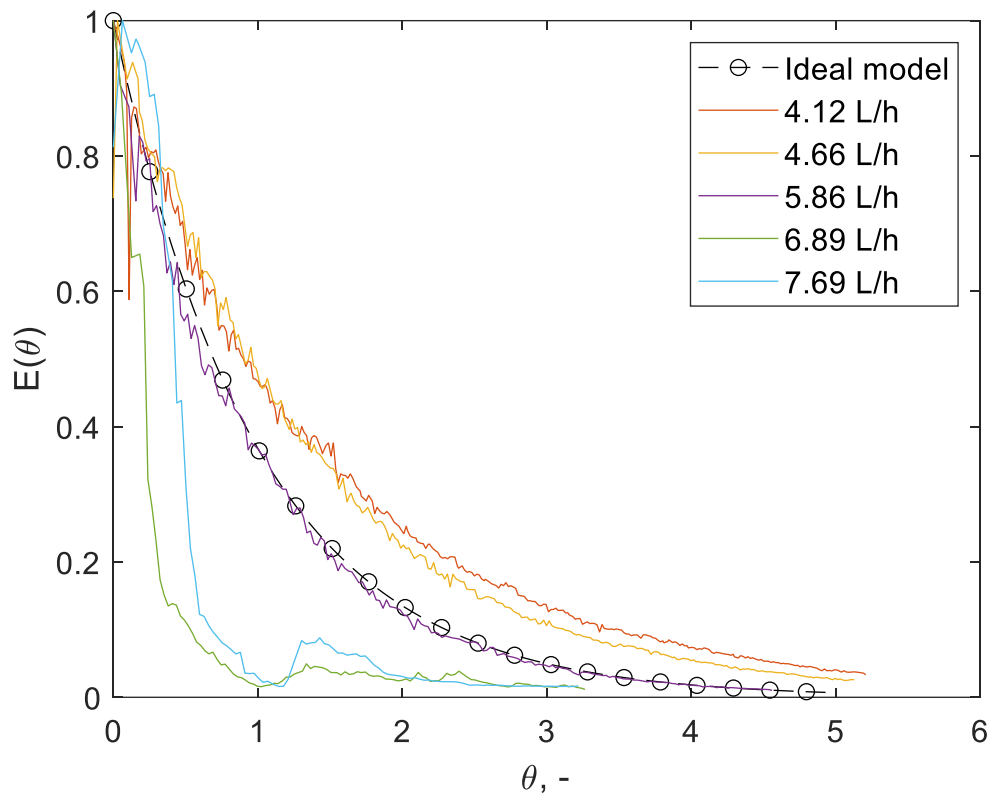


Figure 39. Dimensionless exit time curves for different feed rates compared to ideal curve

DEHPA pulse used was a failed experiment because of too low concentrations, estimation of the KCl concentration can be done from the conductivity curve by using concentration calibration curve (Fig 24). Highest peak in the conductivity pulse tests has KCl concentration of around 0.02 – 0.03 mol/L, and for example in the 8 L/h pulse test mixer KCl concentration reduced to 0.005 mol/L after only 2 minutes.

KCl pulse used was 1 mL with a concentration 3 M, and DEHPA pulse that was 2 mL of 0.8 M. Stronger DEHPA pulse or a step test might provide measurable concentrations.

7.4 Model fitted to the 2-phase aqueous phase data

These results show that the mixer has back mixing in lower feed rates, works nearly ideally around 5.86 L/h and at higher volume flows mixer starts to experience severe bypassing.

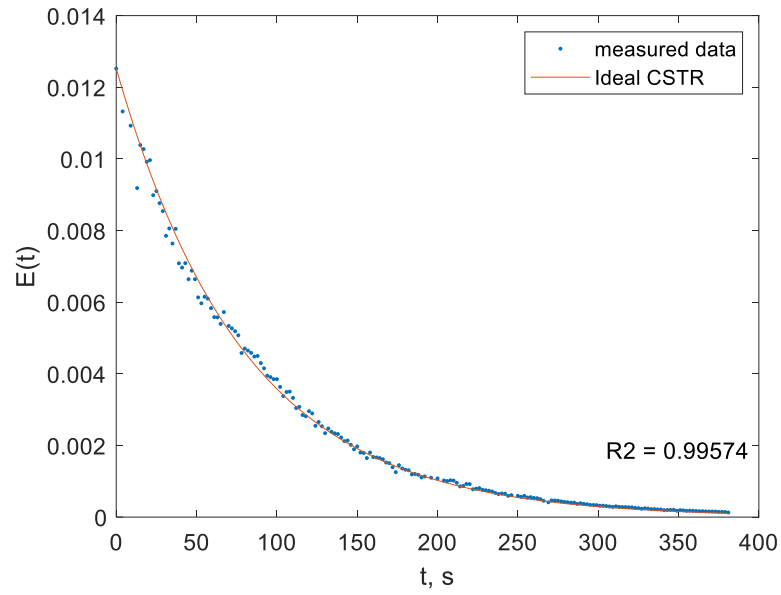


Figure 40. Total volume flow of 5.86 L/h and HRT = 74 s fitted to ideal model

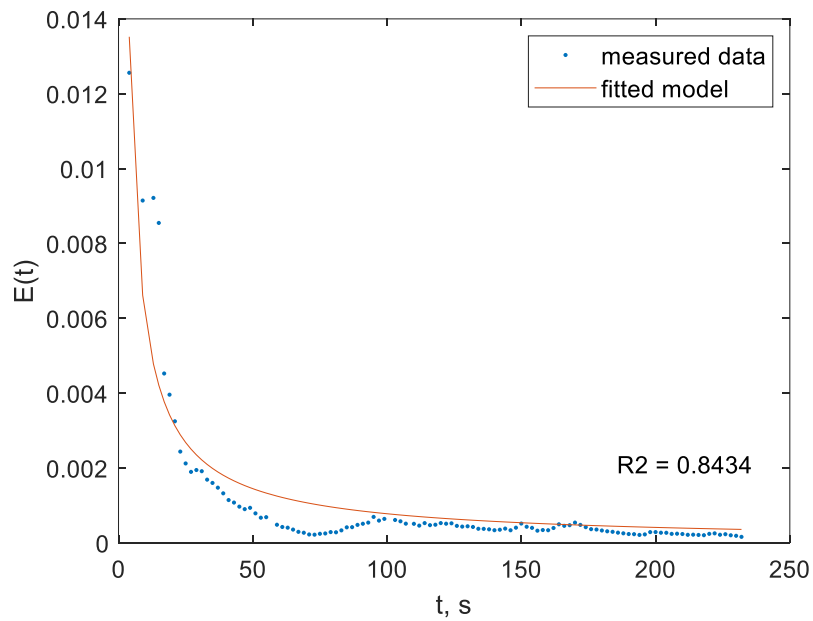


Figure 41. Bypassing model fitted for 7 L/h and HRT of 67 s exit time curve data with a n value of 0.12

Very sharp drop at the beginning was consistent in measurements 7 L/h or higher, so it was concluded to be result of severe bypassing and not measurement error. Data was fitted with bypassing model of $n = 0.1$ and when interpreted with Figure 10. defining bypass fraction, 60% of material exits the reactor in time of 0.1τ which equals to only 7.1 seconds.

Bypassing describes the model well, but model accuracy is somewhat questionable since the drop in conductivity is so radical that there are only a few datapoints at the start of the experiment to fit the model.

Higher volume rates have been reported to lead to lower conversions in previous experiments (Danish, Al Mesfer & Rashid, 2015) (Margi, Yadav, 2020). Definition of bypassing is material leaving earlier than intended and therefore lowering the effective reaction time, which is supported by findings of this thesis.

8 Conclusions

Pulse tracer experiments were carried out for continuous counter-current type bench-scale liquid-liquid extraction pilot reactor to determine residence time distributions, first running the system with only aqueous phase and then with both organic and aqueous phase present. Online conductivity measurements were successful in measuring residence time distributions for aqueous phases, but for organic phase no definitive method analysis method was found to track concentration changes over time.

Both one- and two-phase experiments showed that lower feed rates give suboptimal residence time distribution for aqueous phase. Higher volume flows provide turbulent conditions that improve mixing of the mixer. One-phase experiments showed that high volume flows produced nearly ideal exit time curves, result of turbulence flow of the feed which improved mixing, but this was not the case in the two-phase experiments.

Optimal operating conditions for 2-phase system was found at ~6 L/h where mixer operated nearly as an ideal CSTR, and phases were able to easily separate at the settler. 7 L/h or higher volume flows resulted in a curve that drops drastically indicating high percentage of bypassing flow, which can be linked to loss of conversion reported in literature. Volume flows of 5 L/h or less showed slower exit time curves that can be interpreted as back mixing.

DEHPA used was diluted to 0.8 M and concentrations became too low for analytical methods. Pure DEHPA pulse could be the solution to measure organic phase pulse or feed the DEHPA as a step pulse gradually replacing Exxsol from the system.

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