RESIDENCE TIME DISTRIBUTION: LIQUID PHASE REACTORS

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In this project, the performance of different continuous flow reactors is evaluated and compared to theory by conducting a second-order reaction. To this end, their residence time distribution (RTD) in liquid phase is characterised and different parameters, such as the mean residence time and the dispersion number, are extracted by carrying out tracer experiments. In parallel, the kinetics of the model reaction is determined in a batch reactor.

MAIN TARGETS

- Measure RTD in various continuous flow reactors at different flow rates using pulse and/or step function.
- Carry out a second order reaction and demonstrate the effect of RTD on reactor's performance.

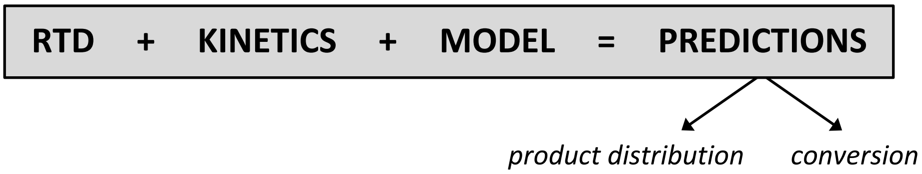
Table of Contents

1. INTRODUCTION

The planning and development of an industrial process requires an optimal strategy in order to maximise the benefits while maintaining a high level of security. As modifications get more and more expensive with the advancement of the project, it is crucial to gather a maximum of information at an early development stage. In this view, first experiments are carried out at a laboratory scale to then go into a piloting phase before being implemented in the production.

For the planning of a chemical process, two aspects are essential; along with a thorough understanding of the chemistry behind the reaction to be scaled up (kinetics and thermodynamics), the fluid dynamics and the thermal behaviour of the reactor have to be characterised. In particular, the fluid dynamics determines the residence time of a molecule travelling through the reactor and the type of molecules encountered during that journey. While many real reactors often exhibit a very different behaviour from their ideal counterparts – plug flow reactor (PFR), continuous stirred tank reactor (CSTR) and batch reactor (BR) –, their performance can be well described using models combining these ideal reactors in series or in parallel.

This section gives an overview of the differences between ideal and real reactors, as well as commonly used theoretical models allowing characterising the behaviour of real reactors. With these models, the performance of a reactor can be predicted for known reaction kinetics:



1.1. Ideal reactors

As mentioned in the previous section, three distinct types of ideal chemical reactors are described in literature:

- Batch Reactor
- Plug Flow Reactor
- Continuous Stirred Tank Reactor

Concentration profiles observed in these ideal reactors [Fig. 1] are obtained by performing simple mass and heat balances. In case of constant temperature and density, the formulas given in Appendix III can be used to establish the link between conversion and Damköhler number,

$$DaI = \frac{\tau}{t_r} \qquad (1)$$

where τ is the residence time and t_r the characteristic reaction time. This parameter, which relates the chemical reaction timescale to the transport phenomena occuring in the reactor, evaluates the degree of conversion achievable for a specific reactor and conditions.

1.2. Real reactors

The behaviour of real continuous reactors varies to a certain extent from ideal reactors. While the CSTR and PFR constitute the perfectly backmixed reactor and the reactor with no backmixing at all respectively, the degree of backmixing achieved in a real reactor depends on several factors, such as the flow regime, dimensions of the reactor, presence of mixers, dead zones and/or shortcuts.

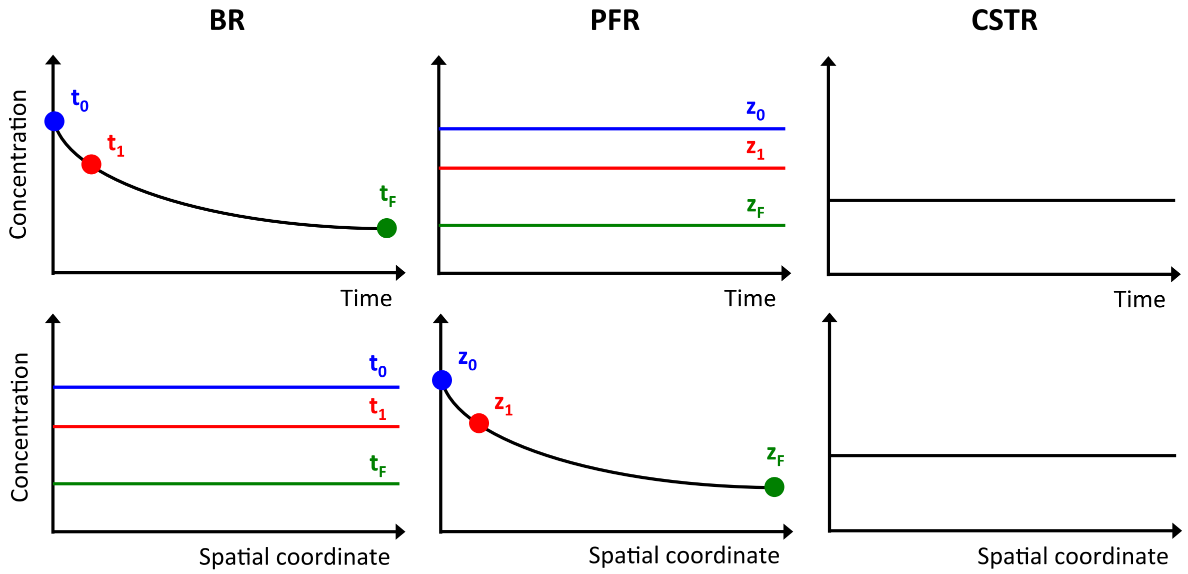


Figure 1. Concentration profiles formed during the reaction in ideal reactors.

To characterise and quantify the deviations of real reactors from ideal models, several methods have been developed. In this project, two models will be applied to evaluate the degree of backmixing in the reactor: the tanks-in-series model and the dispersion model.

Tanks-in-series model

This model is based on a single parameter *N* defining the approximated number of ideal, equally sized CSTRs in series that would be needed to replace the real tubular reactor. The behaviour of an ideal PFR is attained for a cascade of $N = \infty$ CSTRs, whereas perfect backmixing is achieved when $N = 1$.

Dispersion model

In this model, the degree of backmixing is evaluated by means of an axial dispersion coefficient. This lumped parameter contains the backmixing by diffusion and by convection. In dimensionless form, it is defined as the dispersion number,

$$\frac{D_{ax}}{u_{ax} \cdot L} \qquad (2)$$

where u_{ax} is the axial flow velocity, *L* is the reactor length and D_{ax} the axial dispersion coefficient. This parameter characterises the spread in the whole vessel: for negligible dispersion, i.e. when the behaviour of the reactor approaches that of an ideal PFR, the dispersion number is small. By contrast, a large dispersion number reflects a rapid spreading in the vessel. In case of very large mixing, the axial concentration profile disappears and the reactor then behaves as an ideally mixed CSTR. In summary, an ideal CSTR is modelled by $\frac{D_{ax}}{u_{ax} \cdot L} = \infty$, whereas an ideal PFR with $\frac{D_{ax}}{u_{ax} \cdot L} = 0$.

Both dispersion number and number of consecutive CSTRs can be used to predict the performance of a real reactor. Experimentally, these parameters can be derived from residence time distribution measurements.

1.3. Determination of RTD in real reactors

The residence time distribution in real reactors can be estimated by creating a defined concentration signal of inert tracer at the reactor inlet and measuring the response at its outlet [Fig. 2]. In this work, the pulse function and the step function are going to be treated as inlet functions. The treatment of the signal at the reactor outlet will allow determining the dispersion number and the number of CSTRs i.e. the degree of backmixing in the reactor.

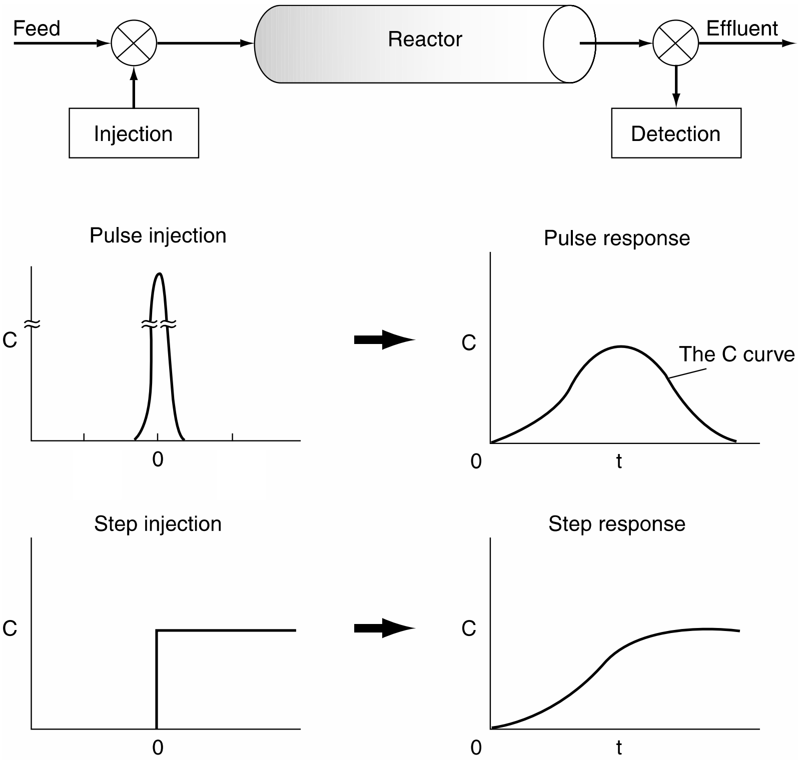


Figure 2. General procedure of RTD measurement.

2. OBJECTIVES

- Carry out residence time distribution (RTD) in various continuous flow reactors at different flow rates using pulse and/or step function. Understand and demonstrate the effect of the following parameters: type of reactor filling, flow rate, stirring speed.
- Evaluate the effect of RTD on reactor performance using a second order model reaction in this case the hydrolysis of ethyl acetate. Before working with this reaction, the kinetics of this reaction is determined in a batch reactor.

3. EXPERIMENTAL

3.1. Experimental setup

The experimental setup comprises three parts: the *200 L* feed tanks, the equipment panel from which the experiments are conducted and the reactors. A scheme of the complete installation can be found in Appendix V and a protocol describing how the whole installation can be operated is detailed in Appendix VI.

Feed tanks

While the installation lies on the ground floor, the feed tanks, containing either water or a sodium hydroxide solution, are located on the second floor to take advantage of the hydrostatic pressure allowing the feed to circulate through the reactors.

Equipment panel

On the equipment panel, the following colors are used to distinguish the chemicals:

- Sodium Hydroxide = Green
- Water = Blue
- Ester = Red (Not used anymore)

The equipment panel allows directing and controlling the flow towards one of the seven continuous flow reactors by means of electronic valves as well as integrated rotameters. The yellow line allows controlling the flow path of the "pumped" liquid.

Reactors

The seven continuous flow reactors available can be divided into two sets:

1. Columns

Three different columns, each filled with different materials, are available: a column containing a static mixer (SMX column), a packed bed column filled with glass Raschig rings and an empty tube [Fig. 3]. Their dimensions are given in Appendix IV. Each column is equipped with a double jacket, which can be heated using a thermostat to control the reactor temperature.

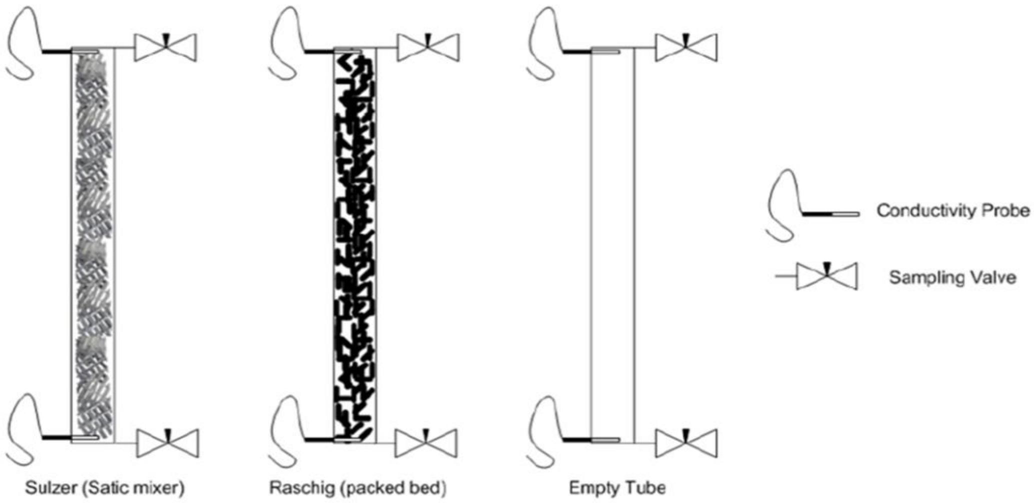


Figure 3. Scheme of the three columns with different fillings

2. CSTRs

One CSTR and a cascade of three CSTR are equipped with a stirrer driven by compressed air [Fig. 4]. Their exact dimensions are given in Appendix IV.

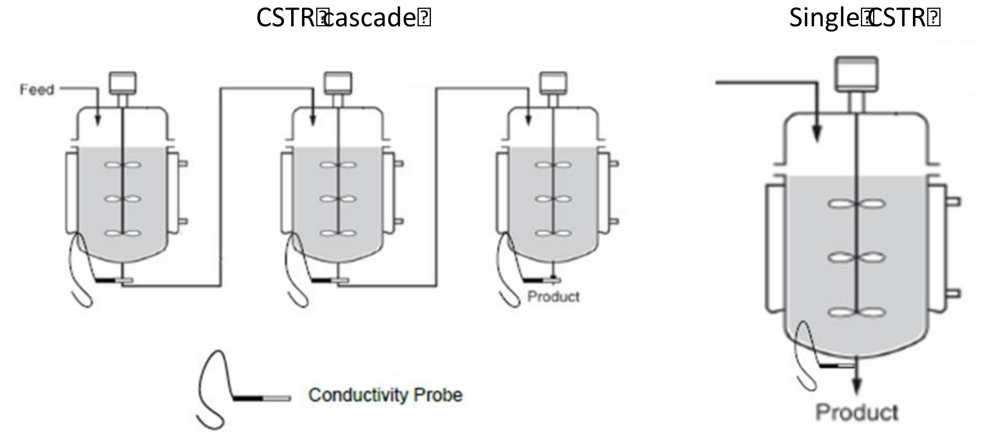


Figure 4. Scheme of the three CSTR in series and the single CSTR

A conductivity probe with integrated negative temperature coefficient (NTC) temperature sensor and a sampling valve is located at the inlet as well as the outlet of each reactor. The conductivity values are obtained by connecting the sensor to one of the two conductivity meters (Labor-Konduktometer 703, Knick). A temperature coefficient of *2 %/°C* is assumed to compensate for temperature effects.

3.2. Model reaction: hydrolysis of ethyl acetate

During the alkaline hydrolysis of ethyl acetate (EA), a *0.1 M* solution of ethyl acetate reacts with *0.1 M* NaOH to yield acetate ions and ethanol:

$$CH_3COOC_2H_5 + Na^+ + OH^- \rightarrow CH_3COO^- + Na^+ + C_2H_5OH$$

The reaction rate r for this second order reaction is

$$r = k \cdot C_{EA} \cdot C_{NaOH} \qquad (3)$$

where k is the rate constant and C_{EA}, C_{NaOH} are respectively the concentration of ethyl acetate and NaOH. The conversion of the reaction is directly proportional to the conductivity of the solution, as the ionic mobility of the small hydroxide ion is much higher than of the bigger acetate ion. Hence, the conversion can be directly determined by conductivity measurements.

3.3. Processing of the experimental data

3.3.1. Residence time distribution

The pulse function

The entire amount of tracer is fed to the reactor inlet within a very short time to approach the Dirac delta function as closely as possible. The Dirac function $\delta(t)$ presents the following properties:

$$\delta(t) = \begin{cases} \infty, & t = 0 \\ 0, & t \neq 0 \end{cases} \qquad \int_{-\infty}^{+\infty} \delta(t)dt = 1. \qquad (4)$$

In practice, the input time *Δt* should be small compared to the space time τ, i.e. $\Delta t < 0.01\,\tau$. The response of the system at the outlet to the pulse-like inlet function is called the C-curve *C(t)* [Fig. 2]. In terms of moles, the amount of tracer *dn* leaving the reactor during a time *[t,t+dt]* is given

$$dn = C(t) \cdot \dot{V}(t) \cdot dt \quad (5)$$

where $\dot{V}(t)$ is the volumetric flow rate. The probability *E(t)* that a molecule entering the reactor at time *t=0* exits the reactor at a time *t* is then simply expressed as the amount of material leaving the reactor $\dot{n}(t)$ normalised by the total number of moles of tracer introduced n_0,

$$E(t) = \frac{\dot{n}(t)}{n_0} = \frac{\dot{V}(t) \cdot C(t)}{n_0} = \frac{\dot{V}(t) \cdot C(t)}{\int_0^\infty \dot{V}(t) \cdot C(t) \cdot dt}. \quad (6)$$

Experimentally, the amount of tracer injected can be determined by measuring its concentration *C(t)* at the reactor outlet,

$$n_0 = \int_0^\infty \dot{V}(t) C(t) dt. \quad (7)$$

In case the volumetric flow rate is independent of time, Equation 6 reduces to:

$$E(t) = \frac{C(t)}{\int_0^\infty C(t) \cdot dt}. \quad (8)$$

The quantity *E(t)* is called the residence-time distribution function and, as for all other variable described by distribution functions, its first moment corresponds to its mean value, in this case the mean residence time $\bar{t}$ of the molecules in the reactor,

$$\bar{t} = \int_0^\infty t \cdot E(t) \cdot dt \, (9)$$

If no dispersion/diffusion occurs along the reactor and for $\dot{V} \neq f(t)$, the mean residence time $\bar{t}$ is equal to the space time $\tau = V/\dot{V}$. In the same way, the dispersion around the mean residence time is given by the second moment of the distribution,

$$\sigma^2 = \frac{\int_0^\infty (t - \bar{t})^2 \cdot C(t) \cdot dt}{\int_0^\infty C(t) \cdot dt}. \quad (10)$$

The step function

The step function is created by a sudden change of inert compound concentration at the reactor inlet [Fig. 2]. The concentration *C(t)* at the outlet is given by the convolution of the inlet signal $C_{in}(t)$ and the residence time *E(t)*,

$$C(t) = \int_0^t C_{in}(t - t') E(t') \, dt'. \quad (11)$$

For a constant input concentration over time,

$$C_{in}(t) = C_0 \qquad t > 0, \quad (12)$$

the cumulative distribution function *F(t)*, known as F curve, is given by the integral

$$F(t) = \frac{C(t)}{C_0} = \int_0^t E(t')\,dt' \quad \Leftrightarrow \quad E(t) = \frac{dF}{dt} \quad (13)$$

As before, the first and second moments of the distribution give respectively the mean residence time and the dispersion,

$$\bar{t} = \int_0^1 t \cdot E(t) \cdot dt \approx \sum_0^1 t_i \cdot \Delta F_i\,, \quad (14)$$

$$\sigma^2 = \int_0^1 (t-\bar{t})^2 \cdot E(t) \cdot dt \approx \sum_0^1 (t_i-\bar{t})^2 \cdot \Delta F_i\,. \quad (15)$$

3.3.2. Models for non-ideal reactors

RTD measurements can then be used to characterise the behaviour of real reactors. While RTD data can be sufficient to predict the conversion of first order reactions, additional information on the mixing occurring in the reactor is required when considering higher order reactions. In these cases, various models based on the RTD measurements and knowledge of the reaction kinetics have been developed to evaluate the performance of real setups. Although the choice of an appropriate model will depend on the reactor characteristics, results obtained from the RTD measurements as well as the structure of the model itself, predictions of the reactor efficiency from several models usually give the limits by which the real experiment is bounded. Here, two different, one-parameter models will be applied to characterise the different reactors used in this project: the dispersion model and the tanks-in-series model.

Dispersion model

As abovementioned, the dispersion model is based on the dispersion number [Eq. 2]. If the deviation from the ideal plug flow is small ($D_{ax}/u_{ax}L < 0.01$ or $\sigma^2 < 0.02$) the following equation

$$\sigma_\theta^2 = \frac{\sigma^2}{\bar{t}^2} = 2\left(\frac{D_{ax}}{u_{ax}L}\right), \quad (16)$$

can be used to extract the dispersion number. Here, θ represents the adimensional time variable, i.e. $\theta = t / \tau$. In this case, the behaviour of the reactor can be regarded as one of an ideal PFR. If the reactor does not behave like an ideal plug flow ($D_{ax}/u_{ax}L > 0.01$) and assuming an open-open system the following model is used:

$$\sigma_\theta^2 = \frac{\sigma^2}{\bar{t}^2} = 2\left(\frac{D_{ax}}{u_{ax}L}\right) + 8\left(\frac{D_{ax}}{u_{ax}L}\right)^2. \quad (17)$$

Tanks-in-series model

The tank-in-series model relates the performance of a real reactor to one of a hypothetical cascade of *N* ideal CSTRs, where *N* is the parameter to be determined from the RTD measurements. Theoretically, the equation describing the residence-time distribution *E(t)* resulting from a pulse experiment performed on a series of *N* CSTRs is

$$E_\theta = \frac{N[N\theta]^{N-1}}{(N-1)!} e^{-N\theta}, \quad (18)$$

with mean residence time corresponding to the space time

$$\bar{t} = \tau, \quad (19)$$

and variance

$$\sigma_\theta^2 = \frac{\sigma^2}{\bar{t}^2} = \frac{1}{N}. \quad (20)$$

In the limit of $N \rightarrow \infty$, the RTD becomes symmetrical and the distribution can then be approximated by a Gaussian function,

$$E_\theta = \sqrt{\frac{N}{2\pi}} exp\left[-\frac{(1-\theta)^2}{2/N}\right]. \quad (21)$$

Experimentally, the parameter *N* is extracted by fitting RTD curves of real reactors by either Equation 18 or 21; the Gaussian approximation [Eq. 21] appears satisfactory for $N > 50$, i.e. when the deviation from an ideal PFR is small. Conversely, when $N < 50$, the fitting should be based on Equation 18. Eventually, if a step experiment is carried out to characterize the reactor, the following fitting function should be used

$$F = 1 - e^{N\theta}\left[1 + N\theta + \frac{(N\theta)^2}{2!} + \cdots + \frac{(N\theta)^{N-1}}{(N-1)!}\right]. \quad (22)$$

For small deviations from an ideal PFR, this model and the dispersion one gives identical results. However, the tank-in-series model can be used with kinetics and can be extended to reactor with recycle.

3.3.3. Theoretical dispersion

In order to compare experimental results to a theoretical model, the dispersion coefficient *D* has to be theoretically estimated. For a laminar flow, the dispersion coefficient is given by

$$D = D_m + \frac{u^2 d_t^2}{192 \cdot D_m}, \quad (23)$$

where D_m is the molecular diffusion coefficient and d_t the characteristic length of the reactor. Upon rearrangement, equation 23 becomes

$$\frac{D}{uL} = \frac{D_m}{u \cdot d_t} + \frac{u \cdot d_t}{192 \cdot D_m} = \frac{1}{Re \cdot Sc} + \frac{Re \cdot Sc}{192}, \quad (24)$$

where shows up the Schmidt *Sc* and Reynolds *Re* numbers,

$$Sc = \frac{\nu}{D_m} \quad (25) \qquad\qquad Re = \frac{u \cdot d_t}{\nu}. \quad (26)$$

Here, ν denotes the kinematic viscosity.

4. SUGGESTED EXPERIMENTS

Reactors' characterization

The mean residence time and dispersion number could be assessed by any or both these methods: pulse experiment (KCl as tracer) and step experiment (NaCl). The experiments could be carried out within a range of flow rates and stirring speeds (for CSTR).

Hydrolysis of ethyl acetate

Taking as model reaction the hydrolysis of ethyl acetate, the performance of the reactors could be compared with theory. Using parameters experimentally found during the RTD measurements and the reaction kinetics, expected conversions could be calculated using both Tanks-in-series and Dispersion model, to then be compared to measured and theoretical ones for different reaction conditions.

5. RECOMMENDED LITERATURE

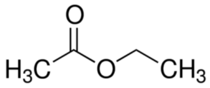
[1] O. Levenspiel, "Flow Patterns, Contacting, and Non-Ideal Flow (Chapters 11-16)", in: Chemical Reaction Engineering, John Wiley & Sons, Inc., 2001.

APPENDIX I. List of symbols and abbreviations

Symbol	Description	Units
$C(t)$	Concentration	[mol/L]
D	Dispersion coefficient	[m^2/s]
DaI	Damköhler number	[-]
D_m	Molecular diffusion coefficient	[m^2/s]
d_t	Characteristic length of the reactor	[m]
$E(t)$	Residence-time distribution function	[-]
$F(t)$	Cumulative distribution function or F curve	[-]
k	Rate constant (second-order reaction)	[L/(mol·s)]
L	Length of the reactor	[m]
n	Number of moles	[mol]
N	Number of ideal, equally sized CSTRs in series required to model a real reactor	[-]
r	Reaction rate	[mol/(L·s)]
Re	Reynolds number	[-]
Sc	Schmidt number	[-]
t	Time	[s]
$\bar{t}$	Mean residence time	[s]
t_r	Characteristic reaction time	[s]
u	Flow velocity	[m/s]
V	Volume of the reactor	[m^3]
ν	Kinematic viscosity	[m^2/s]
θ	Reduced time	[-]
σ^2	Variance	[s^2]
τ	Space time	[s]

Abbreviation	Meaning
BR	Batch reactor
CSTR	Continuous stirred tank reactor
EA	Ethyl acetate
NTC	Negative temperature coefficient
PFR	Plug flow reactor
RTD	Residence time distribution

APPENDIX II. List of chemicals and safety considerations

Sodium Hydroxide	NaOH	
Ethyl Acetate		

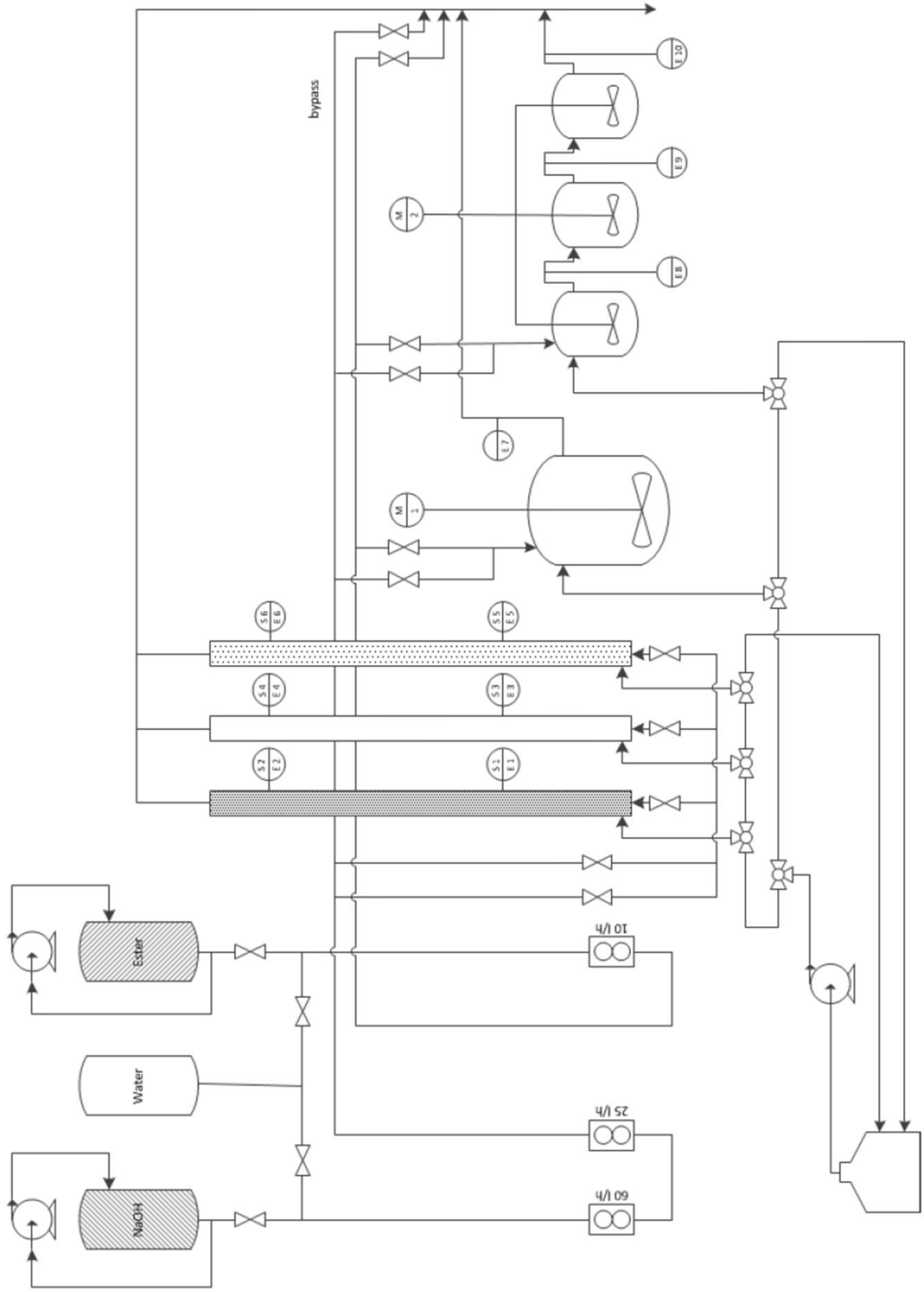
APPENDIX III. Conversion for ideal reactors

cinétique	$DaI=\frac{\tau}{t_r};\ \tau=\frac{V}{\dot{V}_0}$	RM (CSTR)	RT (PFR)
$n \neq 1$ $r = kc_1^n$	$DaI = kC_0^{n-1}\tau$	$DaI_{CSTR} = \frac{X_s}{(1-X_s)^n}$	$DaI_{PFR} = \frac{(1-X_s)^{1-n}-1}{n-1}$
$n = 0$ $r = k$	$DaI = \frac{k}{c_{1,0}}\tau$	$DaI_{CSTR} = X_s$	$DaI_{PFR} = X_s$
$n = 1$ $r = kc_1$	$DaI = k\tau$	$DaI_{CSTR} = \frac{X_s}{1-X_s}$	$DaI_{PFR} = -\ln(1-X_s)$
$n = 2$ $r = kc_1^2$	$DaI = kC_0\tau$	$DaI_{CSTR} = \frac{X_s}{(1-X_s)^2}$	$DaI_{PFR} = \frac{X_s}{1-X_s}$

APPENDIX IV. Dimensions of reactors

REACTOR	d [cm]	L [cm] (entry point to 1st probe)	L [cm] (entry point to 2nd probe)	V_{empty} [L]	Voidage
SMX column	4	64	219	-	0.91
Raschig column	4	64	219	-	0.78
Empty column	4	64	219	-	1
CSTR	-	-	-	4.35	-
CSTR cascade 1	-	-	-	1.95	-
CSTR cascade 2	-	-	-	1.95	-
CSTR cascade 3	-	-	-	1.90	-

APPENDIX V. Installation scheme



APPENDIX VI. Control panel and data acquisition

Before starting, make sure that the tanks containing the solvents you will work with (water or NaOH) are full. When working with the NaOH solution, don't forget to turn on the pump allowing to stir the solution in the tank. **To avoid damages in the installation, keep in mind to regularly check that the reservoirs are not empty while running experiments (check every 1-2h depending on the flow rate used).**

Flow control

All experiments can be controlled from the panel board. To turn it on, switch on position I the three button located at the bottom left of the panel. The flow can then be directed into one of the available reactors by pressing the different control buttons along the desired flow path. Two rotameters (one controlling the flow rate up to 60 L/h and another one allowing a finer tuning for flow rates under 25 L/h) can be used to control the water and NaOH flow rates. To avoid perturbation in the flow, make sure all the columns and CSTRs are filled before doing any experiment with one of the reactors.

Stirring

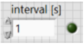
CSTR reactors are equipped with compressed air stirrer. The stirring rate can be controlled using the two roulettes located on the bottom right of the panel (left one for the big CSTR, right one for the CSTR cascade). The stirring rates (in rpm) are indicated on gages located at the top of the CSTRs. Make sure the valve (blue handle) controlling the air flux located behind the control panel is open (if the handle parallel to the line = open, if perpendicular = closed).

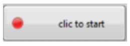
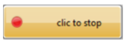
Injection

The injection valves placed at the bottom of the columns are quite sensitive. To avoid them from popping out, hold them tight from top and bottom when injecting.

Conductivity measurements

Two conductometers are available to measure the conductivity of the solutions flowing through the reactors: in the columns, the conductivity can be measured at approximately one third of the column height and at its outlet. In the cascade of CSTRs, the conductivity is determined in the first and the last reactor. Data are recorded using the RTD Recorder software: to do so, the two conductometers are connected to the converter box linked to the computer. To acquire the data:

1) Open RTD recorder software
2) Click ⇨ (run), you can observe the real time data located on the left top of the window and visualize its graph. Ports 1 and 2 correspond to conductometer 1 and conductometer 2.
3) The time interval of data collection can be adjusted according to your needs. 

4) Once the settings are specified, you can start recording the data by clicking on . Then a window pops out asking the file storage path and file name. Note that when you click OK after giving your file name, it starts to record data as time 0.
5) At the end of the measurement, click , the collected data will be automatically saved as text file.

Pump (EA solution)

The hydrolysis of EA is performed by filling the reactor with the NaOH solution and then pump the EA solution from the reactor injection valves. The flow rate provided by EA pump should be measured before use.

Warning: Before leaving the TP hall, make sure you turned off the panel control, closed the compressed air valve, unplugged the conductometers as well as disconnected them from the converter box.