Exercises MRM 2024

The bundle of exercises is under construction. Due to redesign of the course some exercises are still need further updating. Therefore regularly check for an updated version of the bundle.

[1 ODE Solving for reactor modeling 3](#_Toc165587343)

[1.1 First order reaction in a batch reactor 3](#_Toc165587344)

[1.2 Equilibrium consecutive batch reaction 3](#_Toc165587345)

[1.3 Steady state 1D fixed bed reactor model: first order exothermal reaction 4](#_Toc165587346)

[2 Unsteady Convection-Reaction equations 5](#_Toc165587347)

[2.1 Convection of one species using different schemes 5](#_Toc165587348)

[2.2 Multicomponent convection-reaction with first-order chemical kinetics 6](#_Toc165587349)

[2.3 Multicomponent convection-reaction with general chemical kinetics 6](#_Toc165587350)

[3 Implicit convection-diffusion-reaction 8](#_Toc165587351)

[3.1 Solving a one-component 1D diffusion-reaction equation 8](#_Toc165587352)

[3.2 Multi-component 1D counter-diffusion with reaction 9](#_Toc165587353)

[3.3 Multi-component 1D counter-current convection with reaction 10](#_Toc165587354)

[3.4 Convection-dispersion-reaction in a 1D reactor model 11](#_Toc165587355)

[3.5 Particle model: first order reaction 12](#_Toc165587356)

[3.6 Weisz and Hicks model 12](#_Toc165587357)

[4 Modeling Dispersion and Mass Transfer 14](#_Toc165587358)

[4.1 Counter-current column processes 14](#_Toc165587359)

[4.2 Reactor model for heterogeneous bubble columns 14](#_Toc165587360)

[4.3 Kunii and Levenspiel model for a ‘fine particle’ fluidized bed 16](#_Toc165587361)

[4.4 Computing residence time distributions 17](#_Toc165587362)

[4.5 The Westerterp wave-model for axial dispersion in packed beds 18](#_Toc165587363)

[4.6 Modeling a desiccant dryer 19](#_Toc165587364)

[5 2D reactor models 21](#_Toc165587365)

[5.1 Axial convection with radial dispersion 21](#_Toc165587366)

[5.2 Diffusion-reaction in a cylindrical pore 21](#_Toc165587367)

[5.3 2D Membrane Fixed Bed Reactor Model 21](#_Toc165587368)

[5.4 Steady-state 2D fixed bed reactor model: first order exothermal reaction 22](#_Toc165587369)

[5.5 A 2D Gas-solid fluidized bed 23](#_Toc165587370)

[5.6 A 2D Bubble column model 24](#_Toc165587371)

[5.7 Taylor Dispersion 26](#_Toc165587372)

[6 Generalized Maxwell-Stefan equations 28](#_Toc165587373)

[6.1 Ternary diffusion with Maxwell-Stefan equations 28](#_Toc165587374)

[6.2 Dehydrogenation of ethanol 29](#_Toc165587375)

[6.3 Mass transfer limitations using Maxwell-Stefan equations 29](#_Toc165587376)

[8 Advanced reactor modeling 31](#_Toc165587377)

[8.1 Coupled batch reactor and particle model 31](#_Toc165587378)

[8.2 Particle model coupled to column model 31](#_Toc165587379)

[8.3 Pressure-velocity coupling in column models 32](#_Toc165587380)

# ODE Solving for reactor modeling

## First order reaction in a batch reactor

Implement first order kinetics of one species in a batch reactor.

Suggested approach:

* Write a function that computes the reaction rate for a provided concentration
* Write this function in such a way that the reaction rate coefficients can be passed as parameters.
* Provide an analytical expression of the concentration as function of time. Verify your codes with the analytical solution for the case , with initial concentration .

**Questions**:

1. Solve using forward Euler discretization
2. Solve using backward Euler discretization
3. Solve using scipy.integrate.solve\_ivp

## Equilibrium consecutive batch reaction

Implement the kinetics:

Suggested approach:

* Write a function that computes the reaction rate for a provided concentration
* Write this function in such a way that the reaction rate coefficients can be passed as function argument.
* Concentration column vector of length 3 as input (for components A, B, C)
* Reaction rate vector of length 3 as output
* Provide an analytical expression of the concentration as function of time. Verify your codes with the analytical solution for the case , and , with initial concentration , , .

**Questions**:

1. Solve using forward Euler discretization
2. Solve using backward Euler discretization
3. Implement backward Euler discretization, but allow for extension to non-linear kinetics. Express the discretized equations for a time-step as a root-seeking problem for the non-linear set of equations (and use Newton-Raphson).
4. Solve using scipy.integrate.solve\_ivp.

## Steady state 1D fixed bed reactor model: first order exothermal reaction

In a fixed bed catalyst tube of 0.5 m long a heterogeneously catalyzed exothermic (gas phase) chemical reaction takes place. The reaction scheme and associated kinetics are as follows:

where , *Ea*=50 kJ/mol. The reaction is exothermic with –Hr=15 kJ/mol at the reference temperature of 293 K. The molar heat capacities of the gases equal 100, 60 and 40 J/(mol K), for , and , respectively.

Here we will model the reactor as adiabatic. (Of course the reactor should be cooled but this will be considered in a later tutorial). The inlet gas stream consists of pure A and is at a pressure of 1 bar and a temperature 293 K. The interstitial inlet gas velocity equals 2.0 m/s.

**Questions**:

1. Formulate the stationary convection-reaction equations for species , and as well as for the temperature assuming a constant gas velocity.
2. Solve the set of ordinary differential equations assuming constant gas velocity using a standard Python IVP solver.
3. Formulate the stationary convection-reaction equations for species , and as well as for the temperature assuming a constant pressure throughout the reactor. Hint: be cautious about placing the velocity inside or outside of the spatial derivative.
4. Solve this set of ordinary differential equations assuming constant pressure using a standard Python IVP solver.
5. Are the results according to your expectations? Is the temperature increase consistent with the adiabatic temperature rise? Is the increase in velocity in accordance with expectations?
6. Try solving both sets of ODE’s using your own Euler backward solver.

# Unsteady Convection-Reaction equations

## Convection of one species using different schemes

The unsteady convection equation for a concentration that is convected with velocity is:

For unsteady problems we will use the method of lines. After performing a spatial discretization the resulting set of ODE’s has the form:

where is the column vector that contains the concentrations, , where is the label of the grid cell.

You are asked to implement the one-component convection equation using the method-of-lines described above, using different spatial discretization methods, namely, upwind, central differencing and a total variance diminishing (TVD) scheme. For the time integration use a standard IVP solver.

Suggested approach:

* Use NumPy arrays to store the concentrations, , and right hand side, , at different axial positions .
* Prefer using NumPy array indexing notation over for loops for element-wise operations. This approach leverages NumPy’s optimized performance and often results in more readable and efficient code.
* For each method, plot axial concentration profiles for several times.
* Compare your results with an analytical solution of the problem to verify your code.
* Play with the number of grid points used in the spatial discretization.

**Questions**:

1. Implement upwind discretization, where
2. Implement central differencing, where
3. Implement a TVD scheme, e.g. Min-Mod, for the convection. See lecture notes for the scheme.

## Multicomponent convection-reaction with first-order chemical kinetics

In this exercise we will consider the unsteady convection-reaction equation for three components:

where the index refers to one of the 3 components A, B or C. All species move with the (same constant) velocity. The same kinetics as in exercise 1.2 will be used:

For unsteady convection-reaction consider a first order temporal discretization where the convection term is evaluated explicitly (using e.g. a TVD scheme) and the reaction term implicitly:

Here the bold-vector notation is used to indicate column vectors of 3 long where the 3 elements correspond to the 3 species. The subscript indicates the spatial cell and the superscript the time step.

**Questions**:

1. Implement the unsteady convection-reaction equations.

Suggested approach:

* Use a two dimensional array c[i,j] where the first index, i=0,…, N-1, refers to the spatial positions and the second one, i=0,1 and 2 , the index of the species.
* Compute the convection term using the concentration on the old time-step
* Next loop over all grid cells j=1…N and in each cell solve (with ):
* Please, notice how close this is to the problem solved in the second part of exercise 1.2b). Reuse the part of your code developed there.

1. Perform simulations using the same kinetics as in exercise 1.2. Consider an initially empty column of length . At the inlet feed pure A with . Vary the residence time by changing the velocity .
2. Plot concentration profiles in the column for the three species at different times.

## Multicomponent convection-reaction with general chemical kinetics

Consider the same governing equations as in 2.2 but now for general multicomponent kinetics (non first-order). When the convection term is taken explicitly in time values of can be computed from the concentration values of the previous time step, . With the reaction term implicit, we have in each cell the implicit equation

So, for the new concentrations in each cell, a root-seeking problem needs to be solved:

To solve the root-seeking problem, you can use the SciPy method optimize.root, or the newton method from pymrm. For the newton function you need to supply the Jacobian (by means of a function argument that returns and its Jacobian). You can use the function numjac\_local from pymrm to compute the Jacobian. (For optimize.root the Jacobian is optional and needs to be full, while in pymrm we use mostly sparse matrices.)

**Questions**:

1. Repeat the case of exercise 2.2 with this general method. Does it give the same results?
2. Implement a system non-linear reactions. For example:

This is the famous Brusselator (see [Wikipedia](https://en.wikipedia.org/wiki/Brusselator)). Here components and are present in access and thus constant. The kinetics is usually written down in a dimensionless form with all reaction coefficient equal to 1. Suggested inlet concentrations are: , , , and for case two: : , , , .

# Implicit convection-diffusion-reaction

## Solving a one-component 1D diffusion-reaction equation

In this exercise you will build an implicit solver for a diffusion equation. A one-component stationary diffusion equation with constant coefficients has the form

This equation needs to be solved on a domain of length with on the left and right boundaries a boundary condition of the form

where indicates the outward pointing normal direction, i.e. for the left boundary and for the right boundary.

**Questions**:

1. Assume a spatial discretization of cells with points located in cell centers. Write down the spatial discretization formula for the diffusion terms for points . (Note that cells and , are neighboring a boundary).
2. Write down the spatial discretization formula’s for points and by implementing a Dirichlet boundary condition (, ).
3. Write down the resulting formula’s in matrix-vector form.
4. Implement the matrix-vector equation in Python using SciPy. Define a sparse matrix using the SciPy sparse array, e.g., by means of: scipy.sparse.diags\_array.
5. Verify the implementation for Dirichlet BCs on both sides.
6. Extend the boundary condition implementation to general mixed boundary conditions (any value of and ). Write down the resulting formula’s in matrix-vector form.
7. Verify the implementation of the mixed boundary conditions by choosing values of , and on both sides and compare the result with the expected analytical solution.

Dispersion with a first order reaction obeys

**Questions**:

1. Include the first order reaction term to the matrix-vector equation.
2. Verify the implementation for varying values of and general mixed boundary conditions by comparison with the expected analytical solution.

The unsteady diffusion (first order) reaction equation is

**Questions**:

1. Add an implementation of the accumulation term using Euler-backward time discretization.
2. Solve the equations in time and verify the accumulation term by comparison with analytical solutions for (simple) initial and boundary conditions.

## Multi-component 1D counter-diffusion with reaction

Build a model of two reactive components counter-diffusing in a membrane. A chemical reaction is carried out in a membrane reactor. The reaction scheme and reaction kinetics are given as follows:

Reaction kinetics: . The reactants A and B are fed at different sides of a porous membrane. The concentrations on the boundaries are provided in the figure below. For the description of this problem you may assume that the diffusion obeys Fick’s law.

A

cA = 10 kmol/m3

cB = 0

cC = 0

cD = 0

C, D

B

cA = 0

cB = 10 kmol/m3

cC = 0

cD = 0

C, D

y = 0 y = L  
 y

Ceramic membrane

|  |  |
| --- | --- |
| Membrane thickness | 0.01 m |
| Kinetic constant | 106 m3/(kmol s) |
| Kinetic constant | 0 m3/(kmol s) |
| Effective diffusion coefficients of A, B, C and D | 10-5 m2/s |

**Questions**:

1. Write down the governing steady-state equations. For the diffusive term use the notation with a divergence and gradient operator.
2. Write down the spatially discretized equations in terms of matrices corresponding to the discretization of the divergence and gradient operator. Discuss, how the boundary conditions contribute to the discretized equations.
3. The reaction term is non-linear. Formulate the equation to be solved as a root-seeking problem (i.e. a set of non-linear equations that all need equal zero).
4. Formulate the solution algorithm applying the Newton-Raphson method.
5. Provide a Python implementation for the set of equations and its Jacobian using the pymrm building blocks: construct\_grad, construct\_div and numjac\_local.
6. Implement the numerical solution using the newton function from the py\_mrm package.
7. Obtain the steady state solution using Newton-Raphson iteration.
8. Make an unsteady implementation assuming initial zero concentrations.
9. Play with the reaction rates and boundary conditions.

## Multi-component 1D counter-current convection with reaction

Consider the reaction kinetics and boundary conditions as in exercise 3.2 but now with counter-current convection instead of diffusion. Assume that reactant A and product C move from left to right, and reactant B and product D from right to left. One can imagine counter-current liquid and gas flows where some of the components are liquid and others gas. This is modeling a counter-current process where any mass-transfer resistance are neglected.

|  |  |
| --- | --- |
| Reactor length | 1.0 m |
| Kinetic constant | 1.0 m3/(kmol s) |
| Kinetic constant | 0 m3/(kmol s) |
| Velocities |  |

**Questions**:

1. Write down the governing time-dependent evolution equations.
2. Write down the spatially discretized equations in terms of matrices corresponding to the discretization of the divergence and gradient operator. Discuss, how the boundary conditions contribute to the discretized equations.
3. Use backwards Euler time discretization for all terms. Write down the root-seeking problem that needs to be solved. Also provide the Jacobian of the function that needs to be solved.
4. Formulate the solution algorithm applying the Newton-Raphson method.
5. Provide a Python implementation for the set of equations and its Jacobian using the pymrm building blocks: construct\_grad, construct\_div and numjac\_local.
6. Implement the numerical solution using the newton function from the py\_mrm package.
7. Provide the an unsteady solution using Newton-Raphson iteration for each time-step.
8. Play with the reaction rates and boundary conditions. For higher reaction rates, when do numerical issues arise? How can these be resolved. Hint: the pymrm function clip\_approach can be used as a callback function in newton, to make sure that values stay within bounds also inside iterations.

## Convection-dispersion-reaction in a 1D reactor model

In this exercise you will build an implicit solver for unsteady convection-dispersion-reaction equations. A one-component unsteady convection-reaction equation with constant coefficients has the form

The solution method will be the method-of-lines where the spatial dependence is discretized first. After discretization you will get a set of ODE’s that can be written as

Here a component of column vector denotes the concentration is spatial cell . For time-discretization we will use implicit Euler:

**Questions**:

1. Perform the spatial discretization by constructing the sparse matrices for the dispersion and convective terms. Assume a general boundary condition at the inlet,

and a Neumann boundary condition at the outlet

Make use of the pymrm functions construct\_grad, construct\_conv, and construct\_div.

1. Perform the time discretization for the convection-dispersion by means of the implicit Euler scheme, and formulate the problem, without reaction, as a root-seeking problem: for each time step.
2. Provide an Python implementation, that consists of a time-loop, where for each timestep the newton method from the pymrm package is applied to solve the root-seeking problem.
3. Test your code for only dispersion, only convection, combined etc. Play around with parameters (numerical and physical ones).
4. Include a first order reaction term. Compare results to the analytical solution (in a semi-infinite domain) for steady state.
5. Adapt the code for general non-linear kinetics. Make use of the function numjac\_loc to compute the Jacobian of such a reaction term.
6. Verify your code by implementing a reaction kinetics .

## Particle model: first order reaction

Numerically solve the stationary spherical symmetric problem

with .

**Questions**:

1. Perform the spatial discretization (start with a uniform grid) and make a Python implementation. Note that the spherical geometry is accounted for by the proper definition of the divergence operator.
2. Construct, implement and solve the matrix-vector equation.
3. Compute the apparent reaction rate from the concentration gradient on the surface of the particle.
4. Investigate the effectiveness as function of Thiele modulus
5. Does the result correspond to the analytical solution?
6. Consider the high Thiele modulus case and provide an improvement by using a spatial discretization that is refined near the wall.

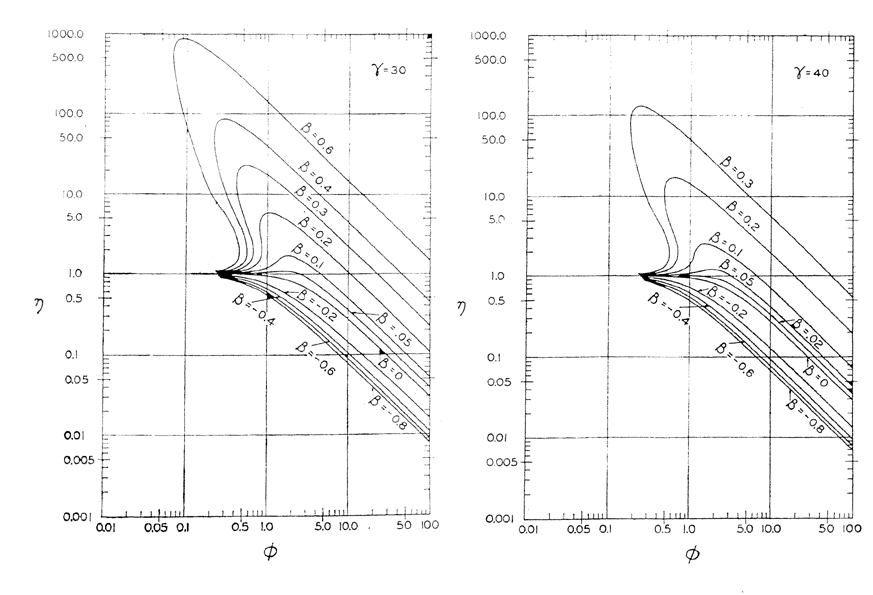
## Weisz and Hicks model

This exercise considers diffusion and reaction in a spherical particle for first order kinetics. The reaction rate, however, is temperature dependent via a Arrhenius dependence.

Assume Dirichlet boundary conditions for both concentration and temperature on the particle surface.

**Questions**:

1. Formulate the model in a dimensionless way by introduction of characteristic numbers , and , Thiele modulus: , (ratio heat generation/transport) and (ratio activation/thermal energy).
2. Provide a Euler-backward Python implementation of both the diffusion and temperature equations.
3. Can you reproduce the case of effectiveness, for a specific choice of , and ?



Source: Chem. Engin. Sc., 1962, Vol. 17, pp. 265-275

Hint: Use a small enough time step to avoid stability issues. Based on the profiles you find, explain what causes the efficiency to be larger than 1?

# Modeling Dispersion and Mass Transfer

## Counter-current column processes

Many (separation) processes, such as absorption, stripping and extraction are often operated in counter-current mode. In this exercise we consider a simple stationary two phase coun0ter-current process for one component with linear driving forces for mass transfer:   
with boundary conditions: ,

Here and are superficial velocities, an overall mass-transfer coefficient and the specific surface area of the interface between the phases and . The coefficient is a distribution coefficient. At phase equilibrium . The driving force of mass transfer is non-zero when there is a deviation from this equilibrium.

**Questions**:

1. Make a Python implementation of the model.
2. **Advanced**: Find the analytical solution of the model. Verify the implementation with the analytical solution.
3. This model can serve as a basis for more advanced modelling of counter-current processes. Consider the implementation of a multicomponent system with a non-linear equilibrium relation between the components in the two phases.

## Reactor model for heterogeneous bubble columns

In this exercise you are asked to model the mass-transfer in a slurry bubble column as proposed by Maretto and Krishna, Catalysis Today 52 (1999) 279-289. In this model the column is described by three phases, two bubble phases, namely, a large and small bubble phase, and a slurry phase. Large bubbles transport gas in a plug flow fashion, and small bubbles have a more turbulent flow pattern that is described in the model as well-mixed. From the bubble phases, gas can dissolve in the slurry phase. This is liquid with suspended particles. Catalytic conversion take place in the particles.

Here we consider the balances of the phases, where subscript labels the large bubbles, *df*, the small bubbles and *s* the slurry:

Although only the steady state is of interest, solving the equations time-dependently might help to find this steady state. Similarly, the dispersion coefficient are numerical parameters, since we are interested in limit values. The bubble phase is modelled as plug-flow, so . For the small-bubble and slurry phases a well-mixed state is assumed. This can be achieved by choosing and large. They should be large enough to have almost no axial profiles for these phases. Note that, there might arise numerical problems when values are chosen very large. The optimal choice can best be determined by a trial-and-error procedure.

In the work of Maretto and Krishna the Fischer-Tropsch reaction is considered, where CO and are aided by the catalyst particles in the slurry to form hydrocarbons. Hold-ups, superficial velocities and mass transfer coefficients follow from correlations. Here we are mostly interested as an exercise to implement the model and investigate its behavior depending on where the main resistance to mass transfer lies.

**Questions**:

1. Implement the slurry bubble column model for one inert tracer species.

|  |  |  |  |
| --- | --- | --- | --- |
| Quantity | Large bubble | Small bubble | Slurry |
| Holdup |  |  |  |
| Superficial velocity [] |  |  | 0 |
| Mass transfer coeff., [] |  |  | - |

1. Determine the cumulative residence distribution for a tracer species introduced in the gas phase. Assume values:

For the distribution coefficient take . Vary the height of the column (up to 30m)

1. Assume that the species is reactive and undergoes a first order reaction at the catalyst particle. Perform a parameter study for the reaction rate coefficient of the first order reaction.

## Kunii and Levenspiel model for a ‘fine particle’ fluidized bed

In reactor models of fluidized beds we usually distinguish different ‘phases’, such as the emulsion phase and bubble phase. Depending on the flow regime, there can be other phases, such as cloud and wake. To construct the reactor model one needs to determine the balance equations for concentrations in each phase, including mass exchange between phases.

In this exercise we will only consider two phases, namely, emulsion and bubble. The emulsion phase is a dense particle phase, where the voidage remains close to the value at minimum fluidization conditions, . At gas velocities above the minimum fluidization velocity, excess gas can create voids, that are referred to as bubbles. For fluidized beds with fine particles (Geldart A), the emulsion phase has a low permeability. This makes that excess gas mostly remains in the bubbles, and that bubbles rise fast relative to the gas velocity in the emulsion phase, .

In this exercise, you are asked to model a catalytic fluidized bed. The particles are catalytically active, so conversion takes place in the emulsion phase, while most gas is transported by the bubbles. The balances for a concentration of gas species in the two phases and can be written as:

We assume that the bubble fraction and the velocities are constant over the height. Note, that if this were not the case one should be really careful about the placement inside or outside of the spatial derivative. The parameter denotes the bubble hold-up. For a specified overall superficial gas velocity, , a total balance for the volumetric flow rate gives:

with and the bubble rise velocity and the superficial gas velocity in the emulsion phase, respectively.

We have a reaction rate only in the emulsion phase. Note that this is an apparent reaction rate that includes potential mass-transfer resistances for transport between (emulsion) gas and particle. The case considered is that of a first order reaction of one species,

In this type of model it is conventional to use volumetrically defined mass-transfer coefficients, based on the bubble volume. This explains the appearing in-front of .

|  |  |
| --- | --- |
| Quantity | Value |
|  |  |
|  |  |
|  |  |
|  |  |
|  |  |

In, the standard text of Kunii and Levenspiel, one can find many correlations for transport coefficients. These are based on theoretical consideration mixed with empirical findings. For example, for the bubble rise velocity in a fine-particle fluidized bed, we have:

where is the bubble diameter and the gravitational constant. In the table we provide numerical values for other key quantities.

**Questions**:

1. Using pymrm functions implement the model for a fine-particle fluidized bed.
2. Compute the conversion as function of height.
3. Investigate the influence of parameters, , , and .

As an aside: For larger particles, Geldart B, the emulsion phase is more permeable. Here excess gas uses the bubbles as a low-resistance shortcut through the bed. Therefore, reactant gas tries to find a low resistance path through emulsion and then through bubble etc. In this case the rise velocity of bubbles is lower than that of the gas in the emulsion phase.

## Computing residence time distributions

An important characterization of flow patterns and mixing characteristics in a chemical reactor are residence time distributions. The cumulative residence time distribution, , can be obtained by measuring the total flow of a non-reactive tracer component at the outlet, starting with an empty reactor at and suppling a constant inlet tracer flux.

**Questions**:

1. Write a routine to output the total outlet flux for a multiphase model.
2. Implement the 1D 1-component unsteady convection-dispersion equation. Use the Danckwerts boundary condition for inflow and Neumann boundary condition at outflow. Implement the dispersive term implicitly. For the convective term you can either choose implicit, explicit, upwind with or without TVD.
3. Investigate the accumulative residence time distribution produced by this model using the written routine. That is, supply a concentration step at the input and measure the fluxes that leave the reactor. Plot the flux that leaves the reactor as function of time, properly normalized such that you get the accumulative residence time distribution, .

The analytical solution, for not too large axial dispersion, is given by

For very large axial diffusion, , the behavior should be CISTR and you have

Compare numerical results with the analytical solution. Investigate both physical and numerical aspects (i.e. time step and grid size dependencies).

1. Model a system with a moving and stagnant phase that exchange mass. In the moving phase both convection and dispersion takes place. One could think of a trickle bed where liquid trickles down, but some liquid close to the packing is stagnant due to capillary forces. Investigate the effect on the residence time distribution due to mass transfer to and from the stagnant liquid.
2. Use the routine to determine the residence time distribution in the next exercise, and for other multiphase models.

## The Westerterp wave-model for axial dispersion in packed beds

Flow profiles in a tube, combined with diffusion in the radial direction can cause dispersion of a solute. The reason is that solute particles experience different flow velocities depending on their radial position within the tube. Particles near the center move faster, while those near the walls move slower. This difference in velocity causes the solute to spread along the length of the tube. This phenomenon is called Taylor dispersion. This is explicitly modeled in exercise 5.7.

In 1D models of a tubular reactor, this dispersion is often mathematically modelled as a diffusive term. This axial dispersion coefficient for a parabolic velocity profile is:

with the molecular diffusion coefficient, the average velocity in the tube and its radius.

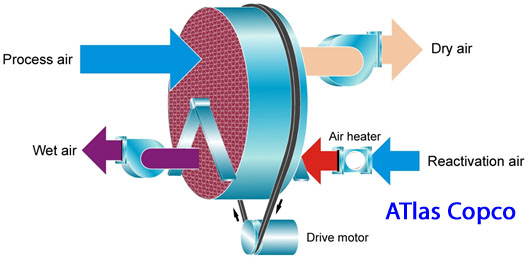
Modelling dispersion using a diffusion term has been criticized. An alternative approach was proposed by Westerterp et al., AIChE Journal 41 (1995) 2013–2028. In this approach Taylor dispersion can be modeled in a 1D model as two phases that have different velocities and mass transfer in between:

**Questions**:

1. Implement a 1D diffusion-convection model, where the diffusion term models Taylor dispersion.
2. Implement the two-phases model of Taylor dispersion.
3. Determine the residence time distributions for the two models for a range of dimensionless Péclet numbers, and aspect ratios .

## Modeling a desiccant dryer

A typical rotating drum desiccant dryer consists of air channels coated by desiccant material. The drum rotates through different air streams in order to dry a process stream and next be regenerated.



The flow of a (humid) gas and simultaneously adsorption of water through a channel can be described by transport equations for mass and heat.

This process can be described by a homogeneous model, where mass and heat transfer resistances between the gas and adsorbent are neglected. Here there is one PDE for humidity in both phases, and also one PDE for temperature:

In these equations is the weight fraction of water in the air stream and the weight of adsorbed water per kg desiccant (a fraction is used because there is also some inert solid material). The first equation expresses a mass balance where the accumulation of water both in air and desiccant is balanced by the transport of water by the air stream. The superficial gas velocity is . The length of a channel is .

In the enthalpy balance the accumulation term has two contribution, one due to heat capacity and next one due to the (lower) enthalpy of adsorbed water. Here is the enthalpy of sorption. This will cause heat to be created when water is adsorbed. Enthalpy is transported along the channel by the gas flow.

The material properties are:

|  |  |  |  |
| --- | --- | --- | --- |
| Material | Densities | Heat capac. | Volume fractions |
| Air |  |  |  |
| Adsorbent |  |  |  |

Locally the water in the air stream is assumed to be in equilibrium with the adsorbed amount of gas. The amount of adsorbed water is related to the relative humidity is described by the following adsorption isotherm: , with and , with K the unit of temperature and Pa the unit of pressure. is the saturation pressure of water at the temperature and the total pressure in the channel. In our case . The heat of sorption per kilogram desiccant is

**Questions**:

1. Implement the model for water weight fraction in air, and temperature, as function of position and time . Suggested approach:
   1. Use a coupled formulation where you solve and simultaneously as component 0 and 1 of a NumPy array.
   2. Evaluate the convection term explicitly using first order upwind (that can be extended later to e.g. min-mod).
   3. The non-linear accumulation term can be treated using Newton-Raphson (using newton from the pymrm package). Compute the Jacobian of the accumulation term numerically (using numjac\_local).
2. Model adsorption of a humid stream with and .
3. Advanced (optional): Simulate, up to cyclic stationary state, of drying and regeneration, as if a drum is rotating through both theses streams. For the regeneration stage the stream enters form the other side. Both stages take 90 seconds, with the inlet conditions of the humid stream: and and the regeneration air stream: and .

# 2D reactor models

## Axial convection with radial dispersion

Implement species transport in a tube with reaction at the tube wall. The governing equation is:

The inlet profile is uniform. Assume an infinitely fast surface reaction at the tube wall. This means . Choose your own parameters or make equations dimensionless.

**Questions:**

1. What is the proper boundary conditions at ?
2. Use the method of lines: Perform a spatial discretization in the radial direction to obtain a set of ODE’s ().
3. Use a standard SciPy ODE solver, solve\_ivp, to solve the set of equations.
4. Compute the flux at the wall as function of .
5. Compute the Sherwood number (based on ) as function of .

## Diffusion-reaction in a cylindrical pore

Simulate diffusion into a cylindrical dead-end pore with infinitely fast reaction on the wall. The pore has radius and length . The diffusion coefficient in both radial and axial direction is

**Questions:**

1. Provide the governing PDE for the two-dimensional diffusion in the pore.
2. What are the proper boundary conditions?
3. Perform the spatial discretization of this (axial symmetric) 2D problem to obtain a matrix-vector equation.
4. Provide a Python implementation.

## 2D Membrane Fixed Bed Reactor Model

In a (single tube) membrane fixed bed reactor a heterogeneously catalyzed chemical equilibrium reaction is carried out. The reaction scheme and associated kinetics are as follows:

The tube wall of the fixed bed consists of a perm-selective membrane through which component selectively permeates. The associated flux expression is given by the following equation:

where represents the effective mass transfer coefficient for the intra-membrane transport and the concentration of component in the sweep gas in the annular zone (see figure below). The concentration of species in the sweep gas can be assumed equal to zero, corresponding to assuming a very large sweep gas flow rate.

D:\Users\eajfpeters\Documents\Teaching\MRM\MRM 2016\Tutorials\fixed_bed.emfThe effective radial dispersion coefficient De,r of all species , , and amounts . The inlet concentration of species and equal 10.0 mol/m3, whereas the inlet concentration of species and are 0.0 mol/m3. In the membrane fixed bed reactor isothermal conditions prevail.

|  |  |
| --- | --- |
| Superficial gas velocity, | 0.2 m/s |
| Inner radius fixed bed tube | 0.02 m |
| Length fixed bed tube | 1.00 m |
| Kinetic constant kf | 0.1 m3/(mol.s) |
| Kinetic constant kb | 0.1 m3/(mol.s) |

**Questions**:

1. Calculate the thermodynamic equilibrium conversion.
2. Formulate the model equations and the associated boundary conditions according to the homogeneous two-dimensional reactor model. Account in your model for the selective permeation of component through the membrane. Neglect axial dispersion effects.
3. Implement the formulated model equations in Python. It is suggested to use a methods-of-line approach where the spatial discretization is performed in the radial direction and the axial dependence is solved using solve\_ivp.
4. For the case of no permeation of () calculate the chemical conversion.
5. Repeat the calculation for part 4 of this problem using values of 0.01, 0.1, 1.0, 10.0 and 100.0 m/s for the effective mass transfer coefficient. Explain the observed differences with respect to the chemical conversion and the obtained radial concentration profiles. Discuss the validity of the model equations for km = 100 m/s.
6. Repeat part 5 of this problem using an effective radial dispersion coefficient of . Discuss the observed results.

## Steady-state 2D fixed bed reactor model: first order exothermal reaction

This is the 2D version of exercise 1.3. In a fixed-bed catalyst-tube of 0.5 m long a heterogeneously catalyzed exothermic (gas phase) chemical reaction takes place. The reaction scheme and associated kinetics are as follows:

where , *Ea*=50 kJ/mol. The reaction is exothermic with –Hr=15 kJ/mol at the reference temperature of 293 K. The molar heat capacities of the gases equal 100, 60 and 40 J/(mol K), for , and , respectively. The (constant) inlet gas stream consists of pure A and is at a pressure of 1 bar and a temperature 293 K. The (constant and uniform) interstitial inlet gas velocity equals 2.0 m/s.

Here we will model the reactor in a 2D fashion. The radius of the tubular reactor is 0.01 m. The reaction is highly exothermic and therefore the catalyst bed needs to be cooled at the wall of the tube. The imposed wall temperature equals 293.0 K. Effective thermal conduction and dispersion are modelled in the radial direction with values and , respectively.

**Questions**:

1. Make a 2D Python reactor model. Note that, because dispersion effects in the axial directions can be neglected, you can use the methods of lines by performing the discretization in the spatial direction and get a set of coupled ODE’s in the axial direction.
2. Calculate the adiabatic temperature rise.
3. Compute the (radially averaged) axial concentration and temperature profiles. Compare the results with the 1D profiles.
4. Compute the exit concentration and temperature profiles. Explain the observed radial temperature profile and explain how the maximum temperature can exceed the inlet temperature augmented with the adiabatic temperature rise.

## A 2D Gas-solid fluidized bed

In a gas-fluidized bed (with diameter and expanded bed height ) heterogeneously catalyzed chemical reactions take place involving the species A, B and C. The reaction scheme and associated kinetics are as follows:

The catalyst material consists of Geldart A type particles with a particle size of 50 m and a particle density of 1500 kg/m3. Additional data are given in Table 1. In the extended Kunii and Levenspiel fine-particle-model the radial gas (bubble) velocity profile is taken into account as well as the radial gas dispersion. For the radial profile of the bubble rise velocity we assume a parabolic profile given by:

where is the average bubble rise velocity. This expression approximately accounts for the fact that the preferential pathway of the bubbles is located in the central part of the gas-fluidized bed. Due to the relatively high value of the average superficial gas velocity the axial gas dispersion can be neglected. Moreover, it can be assumed that the reactor is isothermal. The bubble-to-cloud mass transfer coefficients and the cloud-to-emulsion mass transfer coefficients can be taken the same for the components A, B and C (see Table 1).

**Table 1: Additional data**

- Average bubble rise velocity <U0> : 0.50 m/s

- Reaction rate constant Kr,1 : 0.080 s-1

- Reaction rate constant Kr,2 : 0.010 s-1

- Bubble-to-could mass transfer coefficient Kbc : 2.5 s-1

- Cloud-to-emulsion mass transfer coefficient Kce : 1.5 s-1

- Radial gas dispersion coefficient Di,r (i=A, B and C) : 0.01 m2.s-1

- Bubble phase solids holdup parameter b : 0.005 (-)

- Cloud phase solids holdup parameter c : 0.200 (-)

- Emulsion phase solids holdup parameter e : 5.000 (-)

- Inlet concentration species A: : 5.0 mole/m3

- Inlet concentration species B: : 0.0 mole/m3

- Inlet concentration species C: : 0.0 mole/m3

**Questions**:

1. Formulate the steady state model equations and the associated boundary conditions according to the extended Kunii and Levenspiel Fine Particle Model taking into account the radial profile of bubble rise velocity and the radial gas dispersion.
2. Implement the formulated model equations in Python.
3. Compute the steady state concentration profiles at the outlet of the gas-fluidized bed using the implemented Python model. Inspect the computed concentration profiles carefully and explain the qualitative shape of these profiles. Use 100 radial grid points and 200 axial grid points.
4. Compute the degree of chemical conversion of species A and the selectivity towards the desired product B. Carefully account for the radial gas (bubble) velocity profiles which exist.
5. Consider the case where the bubble rise velocity is uniform and radial gas dispersion can be neglected (assuming uniform inlet conditions). Solve the resulting Ordinary Differential Equations (ODE’s) and compute the degree of chemical conversion of species A and the selectivity towards the desired product B.

## A 2D Bubble column model

In a bubble column the gas hold up is larger in the middle. In rising bubbles induce a circulation pattern, dragging along the liquid in the middle, which circulates downward at the wall. We will model this by using radial profiles of hold-up and velocities. In most of the column these profiles are constant along the height. However, at the bottom and top of the column the flow will also be radially directed. These end zones will be modeled as ideally mixed, such as indicated in the figure below.

|  |  |
| --- | --- |
| A graph of a function  Description automatically generated |  |
|  |
|  |
| Model for a bubble column. For most of the length of the column the flow is purely axial. Radial flow is modeled in an effective way by means ideal mixers in the end-zones. | |

The profiles plotted on the right are measured by means of radioactive particle tracking and taken from Degaleesan et al. (*Ind. Eng. Chem. Res.* **1997**, *36*, 4670-4680). The column diameter is and the height. The flow is in the churn turbulent regime.

From the experimental data plotted in the graphs above we approximate:

We assume that there is difference between the gas-velocity and liquid velocity independent of , such that

The superficial velocity of the liquid equals and of the gas: .

The total height of 190 cm will be divided in 3 parts: a bottom section of 19 cm, a middle section of 152 cm and a top section of 19 cm. The middle section is modeled by means of convection-diffusion reaction equation

Note that we take the turbulent diffusion coefficient of both liquid and gas are taken to be identical. The reason is that (small) bubbles will be dragged along with the liquid.

The top and bottom sections are modeled as ideally mixed. It is advised to model this by using artificially large axial and radial turbulent diffusion coefficients and in these sections. Also make sure that the inflow in the bottom section is actually inflow (i.e., has no negative velocities) and that at the top there is only outflow.

**Questions:**

1. Compute the average hold-ups and determine the values of and such that the prescribed superficial velocities are obeyed.
2. Implement the formulated model equations in Python for the case of insoluble species ().
3. Model a first order reaction in the liquid phase. Hint: Because you consider first-order kinetics the result will be independent of the inlet concentration. A simple choice is . How do the results for a range of kinetic coefficients compare to the conversion in an ideal CSTR and in a plug flow reactor?
4. Model a first order reaction in the gas phase (for a range of kinetic coefficients). How does it compare to the conversion in an ideal CSTR and in a plug flow reactor?
5. Play with the model. Implement a realistic value of , a proper equilibrium relation between gas and liquid concentrations (i.e. ) and interesting kinetics.

## Taylor Dispersion

Taylor dispersion is caused by the presence of a velocity profile. Solute particles experience different flow velocities depending on their (radial) position. By means of molecular diffusion the particles sample these different velocity, which gives a spread in residence time.

The spread of the solute can be described by a 2D convection-diffusion equation:

In a tube with laminar (Poiseuille) flow the velocity profile is

**Questions**:

1. Implement the 2D time-dependent convection-diffusion equations for a cylinder with developed Poiseuille flow.
2. Obtain the molar flow leaving the reactor as function of time and construct a cumulative residence time distribution (RTD from that.
3. Critically compare the RTD with results of the 1D models in exercise 4.5

# Generalized Maxwell-Stefan equations

## Ternary diffusion with Maxwell-Stefan equations

Consider the two-bulb diffusion experiment where bulb A contains a 50-50 molar-% and mixture and bulb B a 50-50 molar-% and mixture. The bulbs are connected by a capillary with length . We will consider the diffusion of the three gasses.

A diagram of a blue circle with text

Description automatically generated

Let’s label the three components as 1: , 2: and 3: . The binary Maxwell-Stefan diffusivities are , and . The pressure and temperature are and , respectively.

The Maxwell-Stefan equations for the first two components can be written as:

Using the constraint and the bootstrap the mole fraction and molar flux of the third component can be eliminated from the set of equation.

**Questions**:

1. Implement and numerically the ODE for the components and using the boundary conditions at : and . Use a shooting method to compute and from the boundary conditions at : : and .

**Hints: In Python you can use SciPy’s solve\_ivp to solve the ODE and SciPy’s root (or newton from pymrm) to obtain and such that the boundary conditions at are obeyed.**

1. Linearize the Maxwell-Stefan equations and compute the fluxes by solving the set of two linear equations.
2. Use the method of Toor, Steward and Prober to solve the ternary Maxwell-Stefan diffusion problem.
3. Numerically solve the problem as a boundary value problem to compute the fluxes and compositions in the capillary (e.g. using the pymrm building blocks).
4. Consider a time-dependent problem where the concentrations in the bulb evolve. The bulb volumes are , . The capillary has cross-sectional area and length . Assume, constant pressures is maintained in the bulbs and ideal gas-law, such that is equal and constant in time throughout the system and . Assume pseudo-steady state in the capillary and use a linearization to compute the flux as function of composition in the bulbs.

## Dehydrogenation of ethanol

Consider the heterogeneously catalyzed reaction:

|  |  |  |  |
| --- | --- | --- | --- |
| ethanol | → | acetaldehyde | + H2 |
| (1) |  | (2) | (3) |

With first order (surface) reaction rate coefficient m/s. The (zero flux) binary mass-transfer coefficients are , and at operating condition and . The bulk gas phase composition 0, and . Assume ideal gases. Assume a film model is appropriate.

**Questions**:

1. Write down the Maxwell-Stefan equations.
2. Solve this system by direct numerical integration. What are the molar fluxes?
3. Solve this system using exact ‘matrix-method’.
4. Make a linear approximation of the concentration profiles and solve the resulting algebraic equations.
5. Solve this system using the approximate ‘matrix-method’ in a mass-average reference frame.
6. Compare the accuracy of the different methods.

## Mass transfer limitations using Maxwell-Stefan equations

We consider the same exothermal catalytic fixed bed 1D column process as in previous exercise 1.3. In this exercise you will investigate the influence of external mass transfer limitations.

In a fixed bed catalyst tube of length the following exothermal reaction takes place in catalytic particles

where , *Ea*=50 kJ/mol. The reaction is exothermic with at the reference temperature of 293 K. The molar heat capacities of the gases equal 100, 60 and 40 J/(mol K), for , and , respectively. The reactor operates adiabatically. The inlet gas stream consists of pure A and is at a pressure of 1 bar and a temperature 293 K. The interstitial inlet gas velocity equals 2.0 m/s.

In the earlier tutorials the effect of external mass transfer limitations from the gas bulk to the active sites on the catalyst surface were neglected, which allowed for a homogeneous reaction rate source term if also intra-particle resistances are small. Now, let’s assume that the catalyst particles are spherical with a uniform diameter of 3.0 mm (bed porosity of 0.4), and that the mass transfer coefficients , are independent of the operating conditions (simplification!).

**Remarks**

* **In this tutorial we consider 3 species only, i.e., there is no fourth inert species. Note, that because the reaction is non-equimolar this would mean in practice that the superficial velocity increases along the reactor length. This effect is neglected in this exercise.**
* **Note that there is a ambiguity in the different exercises on the exact definition of the reaction rate, i.e., is it per m3-reactor, solid or fluid? For the purpose if the current exercise make a convenient choice and make sure your equations are consistent with this choice. Make sure that when you evaluate the influence of mass transfer resistances you compare similar situations, i.e., with the same definitions of the reaction rate.**

**Questions**:

1. Show with a simple estimation whether external mass transfer limitations could be important and should be included in the computations.
2. Formulate the (simplified) equations to account for external mass transfer limitations using the Maxwell-Stefan approach. Make the assumption of linearization of the concentration profiles.
3. Implement the formulated heterogeneous model to account for external mass transfer limitations using the linearized Maxwell-Stefan equations and calculate the axial profiles of the reactant concentration and bed temperature. Assume there are no internal mass transfer limitation.

**Hint: For each species there are now two type of concentrations, namely the concentrations in the bulk of the fluid and the fluid concentrations at the particle surface. There are two approaches to introduce these surface concentrations:**

* + 1. **Only consider these in the reaction term of the column model and eliminate these from the set of equations, such that it returns the apparent reaction rate as function of the bulk fluid concentrations only.**
    2. **Extend the number of variables of unknowns in the column model with the surface concentrations. Solve the set of equations for the full set of variables simultaneously. The equations for the surface concentrations are algebraic.**

**Choose one of the approaches and at the end of the exercise return and attempt the other one.**

1. Verify that the profiles coincide with the results obtained with the homogeneous reaction rate expressions in case the mass transfer coefficients are increased a thousand fold. Compare the axial profiles of the reactant concentration with and without mass transfer limitations and explain the observed differences.
2. Advanced: Formulate the equations to adequately account for external mass transfer limitations using the Maxwell-Stefan approach. Assume that the ideal gas law is valid and use the (exact) matrix method.
3. Advanced: Implement the formulated heterogeneous model with the Maxwell-Stefan equations using the exact matrix method. Compare the results with the linearized solutions.
4. Advanced (optional): Combine the (linearized) Maxwell-Stefan model with the particle-model implementation.

# Advanced reactor modeling

## Coupled batch reactor and particle model

Consider both a batch model and particle model. Inside a particle a diffusion-reaction equation is solved in a spherical symmetric geometry:

with boundary condition

This modeled is coupled to a balance of a batch reactor:

Where the apparent reaction rate can be obtained from the particle model as

**Questions**:

1. Make separate implementations for the particle and reactor model.
2. Verify both implementations. (Think of good critical test cases).
3. Combine the two models such that the particle model can provide the apparent reaction rate for the batch reactor. Use an explicit coupling where, within a time step, you call the models sequentially.
4. Verify the explicit coupling.
5. Provide a implicitly coupled implementation using a ‘Schur compliment’ strategy.
6. Verify the implicit coupling.

## Particle model coupled to column model

Consider both a batch model and particle model. Inside a particle a diffusion-reaction equation is solved in a spherical symmetric geometry:

with boundary condition

This modeled is coupled to a balance of a column:

Where the apparent reaction rate can be obtained from the particle model as

**Questions**:

1. Make separate implementations for the particle and reactor model.
2. Verify both implementations. (Think of good critical test cases).
3. Combine the two models such that the particle model can provide the apparent reaction rate for the batch reactor. Use an explicit coupling where, within a time step, you call the models sequentially.
4. Verify the explicit coupling.
5. Provide a implicitly coupled implementation using a ‘Schur compliment’ strategy.
6. Verify the implicit coupling.

## Pressure-velocity coupling in column models