TRANSPORT EQUATIONS FOR LIQUID PHASE **1**
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Transport equations for liquid phase

Given in cylindrical tube reactor for liquid tube:

Mass:

The molar flux of species i, Wa has two components, the radial component and the axial component, $W_{A,r}$, and $W_{A,z}$, where the molar flow rate is given by:

$$F_{A,z} = W_{A,z} A_{A,z} \tag{0.1}$$

Where $A_{A,z}$ is the cross sectional area of the membrane tube. The molar flux consists of two components, a convective flux and a diffusional flux:

$$W_{A,Z} = j_A + n_A \tag{0.2}$$

where the diffusional flux can be represented with Fick's law, thus:

$$W_{A,Z} = -D_A \frac{\partial C_A}{\partial Z} + v_a C_A \tag{0.3}$$

Similarly, there flux in the radial direction is:

$$W_{A,r} = -D_A \frac{\partial C_A}{\partial r} + v_a C_A \tag{0.4}$$

The mole balance over a cylindrical shell gives for a given specie:

$$-\frac{1}{r}\frac{\partial (rW_{Ar})}{\partial r} - \frac{\partial (W_{Az})}{\partial z} + r_A = \frac{\partial C_A}{\partial t} \tag{0.5}$$

which gives:

$$-\frac{1}{r}\frac{\partial}{\partial r}\left[r\left(\left(-D_A \frac{\partial C_A}{\partial r}\right) + v_r C_A\right)\right] - \frac{\partial}{\partial z}\left[\left(\left(-D_A \frac{\partial C_A}{\partial z}\right) + v_z C_A\right)\right] + r_A = \frac{\partial C_A}{\partial t} \tag{0.6}$$

Simplifying assumptions

1. The convective flux in the radial direction is much smaller than the diffusive flux, thus, $v_{a,r}$ approaches zero and the radial flux will only consist of the diffusive term. $v_r C_A = 0$
2. It is also assumed that the axial velocity, v_z, is constant throughout the tubular reactor and equal to the inlet velocity. Can therefore put the term $v_{a,z}$ outside the axial derivative term (nb! If molar flows is used in axial direction then leave velocity inside derivative).

3. The convective flux is assumed much greater in the axial direction compared to the diffusive flux so the axial flux will only consist of the convective term. $\left(-D_A \frac{\partial C_A}{\partial z}\right) = 0$
4. The system is at steady state. $\frac{\partial C_A}{\partial t} = 0$

With the simplifications, the following equation will represent the component transport on a mole fraction basis:

$$-\frac{1}{r}\frac{\partial}{\partial r}\left[r\left(-D_i c_{tot} \frac{\partial x_i}{\partial r}\right)\right] - v_z c_{tot} \frac{\partial x_i}{\partial z} + r_i = 0 \tag{0.7}$$

Note that the diffusivity term is not constant throughout the reactor if the axial velocity changes radially, eg for laminar Hagen-Poisseille flow. The diffusion coefficient must be kept inside the radial derivative.

In order to obtain the complete description of the acid gas transfer throughout the reactor, a transport equation for all reacting species should be given as well as the product species. For the MEA system a total of 5 transport equations are given.

If a fully developed turbulent flow is developed, all radial effects can be neglected and the problem can be reduced to one of 1-dimension. However, with laminar flow, radial diffusion must be included and it becomes a 2-dimensional problem.

At the reactor outlet ($z = 1$) the average flow rates of all species containing CO_2 is given mathematically as:

$$n_{CO_2,avg,z=1} = \frac{\int_{r=0}^{r=R} (2\pi r) v_r C_{i,r,z=1} dr}{\int_{r=0}^{r=R} (2\pi r) dr} = \frac{\int_{r=0}^{r=R} (2\pi r) v_r C_{i,r,z=1} dr}{\pi r_R^{\ 2}} \tag{0.8}$$

Where i indicates all species containing CO_2.
Similarly, for MEA, the components are MEA, MEACOO-, and HCO3-.

To ensure mass balance of MEA the outlet flux of MEA is integrated as with CO2 but using the grid solutions for the components MEA, MEACOO-, and MEAH+. This should of course be identical to the inlet flux. This test will ensure that the integration is performed correct.

Second test of mass balance is to perform the integration at the inlet ($z = 0$) which must equal the given bulk initial concentrations given from the equilibrium model.

Energy balance

$$-\frac{1}{r}\frac{\partial}{\partial r}\left[r\left(-\lambda_l \frac{\partial T}{\partial r}\right)\right] - v_{z,av} c_{p,l} \rho_l \frac{\partial T}{\partial z} + (-\Delta H_r) r_A = 0$$

Boundary and initial conditions:

The integral expression of the average outlet temperature is given by:

$$T_{L,avg,z=1} = \frac{\int_{r=0}^{r=R} (2\pi r) v_r T_{i,r,z=1} dr}{\int_{r=0}^{r=R} (2\pi r) v_r dr} \tag{0.9}$$

Numerical implementing as an initial boundary problem

Because the axial diffusivity is neglected and since the system is a tubular reactor, the equations can be solved as a 1-dimensional transient problem with cylindrical coordinates, an IVP where the time derivative is treated as a length coordinate.

Gas phase treated as blocks

The simultaneous solution of the liquid phase partial differential equations and the gas phase ode's, gave severe numerical oscillations when the heat and mass interfacial fluxes were coupled. For large interfacial areas the code became unstable and amounted to excessive work for the integrator. The residuals obtained could sometimes not be minimized and led to divergence.

Therefore, the gas phase was treated as blocks that were updated after an incremental section of the liquid phase was integrated. The increments were chosen as described in the next section. The numerical problems encountered earlier for the integrator diminished. However, the successive updating of the gas stream blocks requires a high accuracy of the integrated average fluxes out of each liquid block. Since the reliance of this flux will be governing for the driving forces on the gas side.

The first method used was to integrate directly using a trapezoidal method. This works nicely for adaptive grids and is very fast. However, the accuracy should be checked.

Integrating for the flux directly using eg 0. 8, should be checked since the average outlet velocity is obtained using the trapezoidal method. Should also be normalized, since the differences in quantities are large, by an order of magnitude of up to 9.

Second method was to normalize all vectors prior to the integrator, and to calculate the average outlet concentration first, and then obtain the average flux, using the inlet average axial velocity:

$$n_{i,n,L,avg,z=1} = (C_{i,n,L,avg,z=1} v_{n,z,avg}) = v_{n,z,avg} \frac{\int_{r=0}^{r=R} (2\pi) C_{n,i}(:) v_{n,r}(:) grid(:)_{n,i,r,z=1} d(grid_n)}{\int_{r=0}^{r=R} (2\pi) v_{n,r}(:) grid(:)_{n,i,r,z=1} d(grid_n)} \quad (0.10)$$

For a run with no mass transfer only heat flux.

old:

n_i_in(1)	0.213191313622707
n_i_in(2)	7.63933847819471
n_i_in(3)	1.03042239938440
n_i_in(4)	313.150000000000
n_i_out(1)	0.201550524545337
n_i_out(2)	6.73600731587974
n_i_out(3)	0.908492741635964
n_i_out(4)	313.704888210140

new:

n_i_in(1)	0.213428456351987
n_i_in(2)	7.64783607383230
n_i_in(3)	1.03156858670296
n_i_in(4)	313.150000000000
n_i_out(1)	0.228833684411808
n_i_out(2)	7.64712068697835
n_i_out(3)	1.03339648147132

n_i_out(4) 313.704888210140

- The errors can still be seen in the gas phase as the simulations carries on through the tube. This is due to the trapezoidal method, and a better method should be used. Use a spline for most of the gridpoints and the trapezoidal for the very steep ones at the interphase. The last ones, where most of the gridpoints are located do not carry a large area. For the fewer points with lower gradients, carries a larger area.
- Use 4 order spline, and carry out the integral analytically. This should be more or less just as fast as the trapezoidal.

- Did evaluate the integral of the cubic spline, piecewise polynomial of order 4, after interpolating to the set of datapoints given over the adaptive grid.

Found that the initial trapezoidal method with normalized arrays gave as good or better results at a slightly shorter time interval.

Algorithm for updating incremental gas block.

The interfacial area is defined as: $a_{\text{int}} = \frac{2\pi r_l \Delta z}{\pi r_g{}^2 \Delta z} = \frac{2r_l}{r_g{}^2}$ [m2/m3]

1. get incoming gas fluxes to block, assume ideal gas for now.

$$n_{i,g|j} = p_i / RT \cdot v_{z,g} \tag{0.11}$$

2. obtain outgoing gas fluxes out of block.

$$n_{i,g|j+1} = n_{i,g|j} - R_{i,l|j+1} \tag{0.12}$$

(For inert components, $R_{i,l|j+1} = 0$)

3. outgoing temperature flux block

(0.13)

$$T_{i,g|j+1} = T_{i,g|j} + \frac{dT_g}{dz}\Delta z \tag{0.14}$$

Where, $\frac{dT_g}{dz} = \frac{Q \cdot a_{\text{int}}}{\sum_i c_{p,i,g} n_{i,g}}$

4. obtain new total pressure:

$$P_{g|j+1} = P_{g|j} + \frac{dP_g}{dz}\Delta z \tag{0.15}$$

5. obtain new gas velocity:

$$v_{g|j+1} = v_{|j} + \frac{dv_g}{dz}\Delta z \tag{0.16}$$

Where, $\frac{dv_g}{dz} = -\frac{v_{z,g}}{P_g}\frac{dP}{dz} + \frac{v_{z,g}}{T_g}\frac{dT}{dz} - \frac{RT}{P_g}\sum_k R_{i.l} \cdot a_{\text{int}}$

6. obtain new gas partial pressures.

$$p_{i,g|j+1} = p_{i,g|j} + \frac{dp_{i,g}}{dz}\Delta z \tag{0.17}$$

Where, $\frac{dp_{i,g}}{dz} = -\frac{p_{i,g}}{v_g}\frac{dv_g}{dz} + \frac{p_{i,g}}{T_g}\frac{dT_g}{dz} - \frac{RT}{v_g}\sum_k R_{k.l} \cdot a_{\text{int}}$

7. Update values for new block:

$$p_{i,g|j+2} = p_{i,g|j+1} \tag{0.18}$$

Etc..

After updating the gas phase, these new initial values are used for the next section of the liquid phase.

Alternative method for updating incremental gas block.

The transferred flux to the liquid phase can be subtracted from the gas phase:

1. temperature flux block

(0.19)

$$T_{i,g|j+1} = T_{i,g|j} + \frac{dT_g}{dz}\Delta z \tag{0.20}$$

Where, $\frac{dT_g}{dz} = \frac{Q \cdot a_{\text{int}}}{\sum_i c_{p,i,g} n_{i,g}}$

2. obtain new total pressure:

$$P_{g|j+1} = P_{g|j} + \frac{dP_g}{dz}\Delta z \tag{0.21}$$

3. obtain new gas flux

$$R_{i,g|j+1} = R_{i,l|j+1}\frac{A_L}{A_G - A_L} \tag{0.22}$$

$$n_{i,g|j+1} = n_{i,g|j} - R_{i,g|j+1} \tag{0.23}$$

$$p_{i,g|j+1} = y_{i,g|j+1} \cdot P_{g|j+1} \tag{0.24}$$

While temperature and pressure is updated as is done in the former section. This method will not give the gas velocity directly, however the mass transfer precision will be of the precision of the computer.

Advantages/disadvantages using this method

Due to the numerical oscillations and convergence problems by integrating all the gas phase equations simultaneously, this alternative method, by updating the gas phase incrementally, was though of as a better and faster solution to modelling the tube.

Advantages:

1. This method is faster. The computational cost for the integrator is lower, and the numerical problems earlier encountered are diminished.

Disadvantages:

1. The updating of the gas phase is determined by the incremental length. If the section is divided into too few sections, the gas phase will not be updated accurately. This is especially important for areas where there are large gradients. Also, where the partial pressures goes towards zero, the increments should be sufficiently small to ensure that the partial pressures does not go below zero, but instead goes towards zero.
2. The method relies on accurate integration to obtain the average outlet fluxes. Therefore, the chosen amount of grid-points should be checked with a larger amount to ensure that the calculated outlet fluxes from each liquid phase block are sufficiently accurate. This will be the case for all methods involving a final integration to obtain the average outlet fluxes.

Model comparison with absorber/desorber Fortran model

Compare this model with the absorber/desorber code.

- To compare mass transfer etc., assume same dimensions and use a set interfacial area.
- Set constant mass- and heat transfer coefficients.
- Assume that the radial dispersion is negligible in tube.
- run tube model countercurrent.