Two phase convection diffusion reaction

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December 1, 2020

Introduction

The equations describing a gas-liquid reactor are solved numerically using the finite volume method. Plug flow applies to the gas phase and convection, diffusion and reaction take place in the liquid phase.

Model equations

The mass balance for component A in the gas phase is:

$$\frac{\partial C_{Ag}}{\partial t} = -U_g \frac{\partial C_{Ag}}{\partial x} - \frac{k_g}{H}(C_{Ag} - C_{Ag}^i) \tag{1}$$

Where C_{Ag} is the concentration of component A in the gas phase, U_g is the gas phase velocity, k_g the gas phase mass transfer coefficient, H is the height of the gas phase above the liquid surface, C_{Ag}^i the gas phase interface concentration, x the axial coordinate and t time. The mass balance for component A in the liquid phase is:

$$\frac{\partial C_{Al}}{\partial t} = D \frac{\partial^2 C_{Al}}{\partial x^2} - U_l \frac{\partial C_{Al}}{\partial x} + \frac{k_l}{H}(C_{Al}^i - C_{Al}) + r_A \tag{2}$$

Where C_{Al} is the concentration of component A in the liquid phase, D is the diffusion coefficient, U_l is the velocity of the liquid phase, k_l the liquid phase mass transfer coefficient, H is the height of the liquid phase (note: the height of the gas phase and liquid phase are both H), C_{Al}^i is the liquid phase interface concentration and r_A the reaction rate law. From a mass balance over the gas-liquid interface it follows that the gas phase interface concentration is:

$$C_{Ag}^i = \frac{k_g C_{Ag} + k_l C_{Al}}{k_g + \frac{k_l}{K}} \tag{3}$$

The ratio of the gas phase interface concentration to the liquid phase interface concentration is equal to the equilibrium coefficient K:

$$K = \frac{C_{Ag}^i}{C_{Al}^i} \tag{4}$$

Discretization

Two one-dimensional grids of equal size are used to represent the two phases, one for the gas phase and one for the liquid phase. Central differencing is applied to the diffusion terms and the upwind differencing scheme is applied to the convection terms. Time discretization is fully implicit. The resulting linear system is solved using the Gauss-Seidel method.

Discretization of equations for the gas phase

The discrete form of equation (1) for the first, or left-most, node of the gas phase is:

$$H\Delta x \frac{(C_{Ag,0} - C_{Ag,0}^{old})}{\Delta t} = U_g H \cdot C_{Ag0} - U_g H \cdot C_{Ag,0} - k_g \Delta x C_{Ag,0} + k_g \Delta x \cdot C_{Ag,0}^{i} \tag{5}$$

Where $C_{Ag,0}$ is the concentration of component A at node 0 in the gas phase, $C_{Ag,0}^{old}$ is the concentration of component A of the previous timestep, C_{Ag0} is the inlet gas phase concentration and $C_{Ag,0}^{i}$ is the gas phase interface concentration at node 0. The discrete form of equation (1) for the remaining nodes (second node until the last node) of the gas phase is:

$$H\Delta x \frac{(C_{Ag,j} - C_{Ag,j}^{old})}{\Delta t} = U_g H \cdot C_{Ag,j-1} - U_g H \cdot C_{Ag,j} - k_g \Delta x C_{Ag,j} + k_g \Delta x \cdot C_{Ag,j}^{i} \tag{6}$$

The subscript j denotes values at node j.

Discretization of equations for the liquid phase

Danckwerts boundary conditions apply to the liquid phase. Consequently, an additional node is required for the 'inlet' concentration C_{Al}^{in}:

$$(U_l + \frac{D}{1/2\Delta x})C_{Al}^{in} = U_l \cdot C_{Al0} + \frac{D \cdot C_{Al,0}}{1/2\Delta x} \tag{7}$$

Where C_{Al}^{in} is the concentration of component A at the 'inlet' node, C_{Al0} is the concentration of component A just before the reactor inlet and $C_{Al,0}$ is the concentration at the first liquid phase node. For the first, or left most, node of the liquid phase the discrete form of equation (2) is:

$$H\Delta x \frac{(C_{Al,0} - C_{Al,0}^{old})}{\Delta t} = -DH\frac{C_{Al,0} - C_{Al}^{in}}{1/2\Delta x} + DH\frac{C_{Al,1} - C_{Al,0}}{\Delta x} + U_l H \cdot C_{Al}^{in} \\ - U_l H \cdot C_{Al,0} + k_l \Delta x(C_{Al,0}^{i} - C_{Al,0}) + r_A H \Delta x \tag{8}$$

Where $C_{Al,0}^{old}$ is the concentration of component A at node 0 of the previous timestep and $C_{Al,0}^{i}$ the liquid phase interface concentration at node 0. For 'central' nodes the discrete form of (2) is:

$$H\Delta x \frac{(C_{Al,j} - C_{Al,j}^{old})}{\Delta t} = -DH\frac{C_{Al,j} - C_{Al,j-1}}{\Delta x} + DH\frac{C_{Al,j+1} - C_{Al,j}}{\Delta x} + U_l H \\ \cdot C_{Al,j-1} - U_l H \cdot C_{Al,j} + k_l \Delta x(C_{Al,j}^{i} - C_{Al,j}) + r_A H \Delta x \tag{9}$$

The subscript j denotes node j. Concentration gradients at the liquid phase outlet are set to zero. Therefore the discrete form of (2) for the final node (node $n-1$) is:

$$H\Delta x \frac{(C_{Al,n-1} - C_{Al,n-1}^{old})}{\Delta t} = -DH\frac{C_{Al,n-1} - C_{Al,n-2}}{\Delta x} + U_l H \cdot C_{Al,n-2} - U_l H$$
$$\cdot C_{Al,n-1} + k_l \Delta x (C_{Al,n-1}^i - C_{Al,n-1}) + r_A H \Delta x \tag{10}$$

The terms in equations (8) to (10) containing the reaction rate law need to be linearized:

$$r_A = r_A^* + \frac{\partial r_A^*}{\partial C_{Al}}(C_{Al} - C_{Al}^*) \tag{11}$$

The asterisk denotes values from the previous iteration.

Ideally mixed liquid phase

It is interesting to compare the results obtained from solving (5) to (10) in the limit where the diffusion coefficient D is large with those obtained assuming the liquid phase is ideally mixed. In the case when the liquid phase is ideally mixed a mass balance over the liquid phase gives:

$$HL\frac{\partial C_{Al}}{\partial t} = U_l H \cdot C_{Al0} - U_l H \cdot C_{Al} + \int_0^L k_l(C_{Al}^i - C_{Al})dx + r_A HL \tag{12}$$

Where L is the length of the reactor. Since the liquid phase is ideally mixed it can be represented by a single node. The discrete form of equation (12) for this single node is:

$$HL\frac{(C_{Al} - C_{Al}^{old})}{\Delta t} = U_l H \cdot C_{Al0} - U_l H \cdot C_{Al} + \sum_{j=0}^{n-1} k_l(C_{Al,j}^i - C_{Al})\Delta x + r_A HL \tag{13}$$

The term containing the reaction rate law needs to be linearized, as before. Equation (13) is then combined with equations (5) and (6) and the resulting linear system is solved for various values of the system parameters. These results are then compared with the results obtained from solving (5) to (10) for large values of the diffusion coefficient. To facilitate the oncoming discussion the linear system represented by (5), (6) and (13) is named model 1 and the linear system represented by (5) to (10) is named model 2.

Verification

In order to verify that the computation proceeds correctly it is verified that equations (5), (6) and (13) of model 1 and equations (5) to (10) of model 2 are satisfied. Analysis shows that the equations are satisfied with an error in the order of 1e-15.

Results

A comparison of the results obtained from model 1 with results obtained from model 2 is given in table 1. All parameter values (k_l, k_g, U_g, U_l, L, etc) were set to 1, except the equilibrium coefficient which was set to 2, the height H which was set to 0.5 and the reaction rate constant which varied. The diffusion coefficient present in model 2 was set to an arbitrary large value, in this case 1e+3. 10 nodes are used along the x-coordinate and 20 timesteps are taken. A total of 1 s is simulated and the starting time was 0 s. The reaction rate law used for comparison is:

$$r_A = -k_r \frac{C_{Al}^2}{1 + C_{Al}} \tag{14}$$

Results show that the liquid concentrations obtained from solving the equations of model 1 are the same as those obtained from solving the equations of model 2. From this it can be concluded that as the diffusion coefficient grows large the behavior of the liquid phase of the convection diffusion model approaches the behavior of an ideally mixed phase. Note though that this is only true if Danckwerts boundary conditions apply.

Table 1: Comparison model 1 and model 2

k_r	C_{Al} model 1	C_{Al} model 2
1.0	0.1309	0.1309
5.0	0.1203	0.1203
10.0	0.1100	0.1100
25.0	0.0900	0.0900
100.0	0.0556	0.0556
500.0	0.0273	0.0273