# CYCLIC ADSORPTION SIMULATOR

Flow is positive in positive direction z (m), cross sectional flow area of bed is A (m2). The bed is a fixed bed of beaded adsorbent particles. In this version we have two beds and we solve for both beds simultaneously.

##### 1.1 Conservation of Mass

In a bed the conservation of mass for species i is (axial flow though uniform area bed).

, i =1 to N-1 1.1

The conservation of total mass is:

1.2

The total gas concentration is:

1.3

The relationship between gas concentration and pressure, temperature, and mole fraction (yi) is:

1.4

We only need to have N-1 species conservation equations to calculate Ci since the last one can be found from equation 1.3. Its best to calculate the most concentrated species by difference since calculating the trace component this way may lead to error.

The velocity as written on the right-hand side in equation 1.1 and 1.2 is the superficial velocity, where q is the local volumetric flow rate (m3/s) and A the projected flow area in the direction of flow (m2). Overall bulk density of the bed = , kg/m3and accounts for internal particle voidage and bed voidage. Loading of species is based on a unit mass of adsorbent.

Units of the above are:

=contactor bulk density, kg/m3

T = temperature, K

C = concentration of gas, mol/m3

P = pressure, Pa

ni = loading of species i on the adsorbent (mole/kg or mmole/g)

Ci = concentration of species I in the gas, mol of i/m3

= superficial gas velocity, m/s

= bed voidage

##### 1.2 Conservation of Energy

The conservation of energy, assuming the adsorbent and gas phase are **locally** in thermal equilibrium is:

1.5

Here we have allowed for an internal heat generation rate per unit mass of bed (example electrical heating or internal heat transfer) and cooling rate such as through an internal cooling coil or heat loss to the environment.

Units are:

= contactor specific heat, J/kg. K

T = temperature, K

= isosteric heat of adsorption of i, J/mole i

= rate of internal bed heating, J/kg.s or W/kg

= rate of internal bed cooling, J/kg.s or W/kg

=gas specific heat, J/mol. K

The gas specific heat may be found from

1.6

Each term in the energy equation has units of J/m3.s

##### 1.3 Conservation of Momentum

The conservation of momentum is reduced to bed pressure drop only – ignore other momentum changes:

For a packed bed, the Ergun Equation is used:

1.7

Units:

bed pressure, Pa

z = bed axial position, m

= superficial gas velocity, m/s

= gas viscosity, Pa.s

= particle diameter, m

= gas density, kg/m3. This can be obtained from the ideal gas equation:

where M is the molecular weight of the gas obtained as where mi are molecular weights of species i and yi is the mole fraction.

##### 1.4 Other relationships

###### Rate of adsorption:

We use the Linear Driving Force based on solid diffusion:

, i=1 to N 1.8

where the linear driving force rate constants ki will depend on many factors such as T,P,ni etc and may be different between adsorption and desorption (depends on the sign of ). We may need a separate subroutine for ki.

###### Equilibrium Isotherms:

Three isotherm equations are available:

1. Simple linear adsorption

1.9

where where DHi is the isosteric heat of adsorption

1. Single site Langmuir Equation

For single species

1.10

In a mixture:

1.11

The isotherm parameters b are dependent on temperature as where dHi is the isosteric heat of adsorption. The parameters mi are constant.

1. The Dual-site Langmuir Equation (DSL):

For single species

+ 1.12

In a mixture:

+ 1.13

###### Gas Equation of State:

We assume ideal gas behaviour hence

1.12

1.13

###### Isosteric Heat of Adsorption

While we could calculate the isosteric heat of adsorption rigorously from the Clausius-Clapeyron equation but this adds extra computation time so we will use constant values here given the relative errors involved. Later versions can correct this with a rigorous calculation

###### Voidage and Density Relationships

 = bed voidage (does not include voids in the adsorbent particles) used for flow purposes and pressure drop

ads = adsorbent particle voidage – this is the porous voidage within the beads of the adsorbent

t = total voidage =  + (1-) \*ads,

ads = adsorbent density (not contactor density), kg/m3

###### Boundary conditions

At either end of the contactor, the flow enters or leaves as determined by the connectivity to the bed and the status of the valves at either end of the bed. The flow is either specified from an upstream condition (valve CV and upstream pressure) or is calculated from the bed condition and a downstream condition. Similarly, the composition is either as determined from an upstream gas stream or the z=0 or z=L composition in the bed. If the bed is connected to a pump then the flow curve must be used.

##### 1.6 Numerical Implementation – finite volume implantation.

###### Dependent variables:

The unknowns are

1. the concentration of species i in the bed as a function of z and t.
2. the temperature and total gas concentration in the bed as a function of z and t
3. the solid loadings of species i in the bed as a function of z and t

We use the finite volume method to discretise the spatial derivatives. This is preferred over the finite difference method (or finite element) because it inherently conserves mass regardless of the level of discretisation. The centre of each finite volume is denoted cell s while the upstream and downstream faces are s-1/2 and s+1/2 respectively. We have a total of NS number of nodes

1/2 1 3/2 2 5/2 .....s-1/2 s s+1/2 .....NS-1/2 NS NS+1/2

If we integrate (1.2) across a volume we get:

1.14

Therefore we get;

1.15

Equations (1.8) become (for each volume s):

1.16

We calculate the change in concentration of species i from integration of (1.1) across each finite volume:

1.17

gives

1.18

From 1.12:

1.19

And the pressure derivative is given by the appropriate pressure drop expression such as the Ergun equation. Integrating 1.19 over element s gives:

1.20

In general, ;

1.21

Where is the average value of the pressure gradient in volume s.

To solve for the temperature profile, we need to integrate 1.5 across a finite volume s:

1.22

This gives:

1.23

**This completes the set of equations for conservation of mass and energy for the bed. The equations need to be cleaned up and recast in the form of a set of ODE’s before solving.**

Dividing 1.15 by gives

1.24

Also

1.25

1.26

1.27

Equations 1.24 to 1.27 forms a set of ODEs in the vector . Once these values are returned at each node s for each time step, we can determine the local bed pressure with equation 1.21 and the mole fraction of each species from 1.13. Note that we need wall values ( or *s*-1/2) for as these variables are convected from one node to the next and we also need velocity to form the right-hand side of the set of ODE’s which we can get from solving the Ergun equation backwards ie from the known pressure profile, obtain the gradient and then solve for velocity. The total number of equations are 2\*(NS \*(1+2\*N)) where NS is the number of finite volumes and N is the number of gas species. There are two beds so the total is multiplied by 2.

###### Calculating wall values and Flux Limiters

In equation (1.24, 1.26, 1.27) we need to calculate wall values ( or *s*-1/2) for . To determine the value at each face, we need to use some flux interpolation scheme. There are many options for interpolation of the node values to get the wall values. A simple upwind scheme declares that the wall value is the same as the upstream node value, depending on the direction of flow. This scheme is stable, very fast to compute, but not very accurate and in most adsorption simulations is not good enough (it works well for DAC which is very dispersed). Lets include two options:

Option 1: Upwind interpolation for wall values for any variable y which is known at nodes s and s +1 is:

1.28

Option 2: The advantage of high-resolution numerical schemes is a precise interpolation between cell averages to cell walls with the aim of reconstructing these flux terms in such a way that accuracy and stability are maintained as much as possible. This option uses the generalized form of Koren’s interpolation for general variable y:

1.29

Where is the ratio of consecutive flux gradients

1.30

We useto avoid division by zero. The flux limiting function is given by Sweby as:

1.31

Once the ODE’s have finally been assembled, an appropriate ODE solver routine is called to return the solution at the next desired time interval.

##### 1.6 Boundary conditions

At each time step, the conditions at each end of the bed (z=0 or z=L) depend on the valve conditions. The following options must be catered for:

Z=0:

Case 1: The valve opens between a bed at z=0 and a vessel maintained at constant pressure. The flow rate to the bed at z=0 is given by a pressure drive flow through the valve between the vessel pressure and the bed pressure at z=0. The temperature and composition of the gas is specified as the instantaneous vessel temperature and composition.

Case 2: The valve is a mass flow controller and opens between a bed at z=0 and a vessel maintained at constant pressure. The flow rate to the bed at z=0 is given by the value of the mass flow controller (specified either as mole/s or kg/s). The temperature and composition of the gas is specified as the instantaneous vessel temperature and composition.

Case 3: There is no flow (all valves are closed at z=0). The bed conditions at z=0 are determined by backwards extrapolation from the first node and apply zero velocity at z=0 to ensure the Ergun equation is satisfied.

Case 4: The valve opens between a bed at z=0 and a compressor. The flow rate to the bed at z=0 from the compressor is determined by the compressor curve which is the actual volumetric flow rate (m3/hr) as a function of discharge pressure (P at z=0). This flow rate is converted to a molar flow rate using the ideal gas equation and the calculation of velocity is the volumetric flow rate divided by eth cross sectional area. The temperature is specified as a given value. The temperature and composition of the gas is specified as it usually originates from an upstream operation and is considered constant.

Case 5: The valve opens between a bed at z=0 and another bed at its z=0 position. The flow rates between the beds at z=0 is given by a pressure drive flow through the valve between the beds. The temperature and composition of the gas is the instantaneous value of the gas leaving one bed and entering another.

Case 6: The valve opens between a bed at z=0 and a vacuum pump. The flow rate from the bed at z=0 to the vacuum pump is determined by the vacuum curve which is the actual volumetric flow rate (m3/hr) as a function of suction pressure (P at z=0). This flow rate is converted to a molar flow rate using the ideal gas equation and the calculation of velocity is the volumetric flow rate divided by eth cross sectional area. The temperature is specified as a given value at z=0. The temperature and composition of the gas is that occurring at z=0.

The same 6 cases apply to conditions at z=L.

###### Additional Equations

In addition to solving for the profiles in the bed, it is useful to perform mass and energy balance calculations to confirm that all error tolerances are sufficiently small and to provide data on moles of each species entering and leaving the bed after each valve switch. This can be done as a post processing step. Additional equations may be required to keep track of the flows and compositions into and out of vessels especially if the vessels are not constant pressure

##### 1.6 Nomenclature

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Variable Name** | **Description** | **Units** | **Program name** | **Calculated or constant** |
|  | Total gas concentration | mol/m3 | y(1) -> y(n)  where n is number of finite volumes | calculated |
|  | Concentration of CO2 in gas phase | mol/m3 | y(1+n)-> y(2n)  where n is number of finite volumes | calculated |
|  | Concentration of H2O in gas phase | mol/m3 | y(1+2n)-> y(3n)  where n is number of finite volumes | calculated |
|  | Concentration of air | mol/m3 |  | calculated |
|  | Loading of CO2 on the adsorbent | mol/kg | y(1+4n)-> y(5n)  where n is number of finite volumes | calculated |
|  | Loading of H2O on the adsorbent | mol/kg | y(1+5n) -> y(6n)  where n is number of finite volumes | calculated |
|  | Loading of CO2 on the adsorbent at equilibrium | mol/kg | eq\_CO2 | calculated |
|  | Loading of H2O on the adsorbent at equilibrium | mol/kg | eq\_H2O | calculated |
|  | Bed voidage (typically 0.37) | none | parm.con\_void | constant |
|  | Contactor bulk density | kg/m3 | parm.dens\_con | constant |
|  | Bed superficial velocity | m/s |  | calculated |
|  | time | s | t | variable |
|  | Bed length variable | m | z | variable |
| *L* | Total bed length | m | parm.contactor\_length | constant |
|  | Contactor heat capacity (includes support) | J/kg.K | parm.cp\_con | constant |
|  | Temperature | K | y(1+3n)-> y(4n) | calculated |
|  | Isosteric Heat of Adsorption for CO2 | J/mol | parm.Hads\_CO2 | constant |
|  | Isosteric Heat of Adsorption for H2O | J/mol | parm.Hads\_H2O | constant |
|  | Rate of heat generation | W/kg | parm.heat\_rate | constant |
|  | Gas heat capacity | J/mol.K | parm.cpg  parm.cvg | constant |
|  | Pressure | Pa | parm.p | calculated |
|  | Mole fraction of CO2 | none |  | calculated |
|  | Mole fraction of H2O | none |  | calculated |
|  | Ideal Gas Constant | 8.314462618 SI units | parm.R | constant |
|  | Number of finite volume nodes | none | parm.node | constant |
|  |  |  |  |  |
|  |  |  |  |  |
|  |  |  |  |  |
|  |  |  |  |  |

### DAC MODEL - ADSORBENT

For amine loaded adsorbents, it is often preferable to use a different model from DSL. A standard isotherm model used to describe CO2 adsorption on amine-functionalised adsorbents is the temperature-dependent Toth isotherm which has previously been used for amine functionalised silica, cellulose, and Lewatits VP OC 1065, the latter increasingly being regarded as a benchmark DAC adsorbent. A different adsorption isotherm is used to model water adsorption.

#### CO2 Adsorption

The temperature-dependent Toth isotherm is an empirical extension to the Langmuir isotherm which improves the fit at the lowest and highest-pressure range.

where:

= loading of CO2, mol/kg

= maximum CO2 capacity, mol/kg

= affinity of CO2 to the adsorbent, 1/Pa

= partial pressure of CO2, Pa

= exponential factor to account for surface heterogeneity

The maximum CO2 capacity is defined by:

where:

= at the reference temperature T0(K)

T = temperature, K

a factor used to describe temperature dependency

The affinity of the sorbent to CO2 is defined by

Where:

=pre-exponential affinity parameter, 1/Pa

=isosteric heat of adsorption, J/mol

R = 8.314 J/mol/K = Universal gas constant

The surface heterogeneity is defined by

Where:

= at the reference temperature

 = factor used to describe temperature dependency

#### Water Adsorption:

Water on silica adsorbents and amine-silica adsorbents typically follows a Type III isotherm. We choose an isotherm model commonly used to describe this behaviour, the GAB model:

Where:

= loading of water, mol/kg

= loading that corresponds to a monolayer, mol/kg

k = affinity parameter (dependent on T)

c = affinity parameter (dependent on T)

x = relative humidity

Where:

E1 = heat of adsorption of the first layer of adsorption, J/mol

E10+ = heat of adsorption of the 10th layer and higher, which is equivalent to the latent heat of condensation of water, J/mol

Where:

E2-9 = heat of adsorption of the 2nd to 9th layer, J/mol

Up to 100°C, the thermal stability limit of Lewatit, the heat of condensation of water can be modelled as:

And

#### Effect of humidity on CO2 adsorption:

On amine-functionalised adsorbents, it has been shown that CO2 has little impact on H2O equilibrium up to RH of at least 60%. However, H2O enhances CO2 adsorption significantly. The three major effects are:

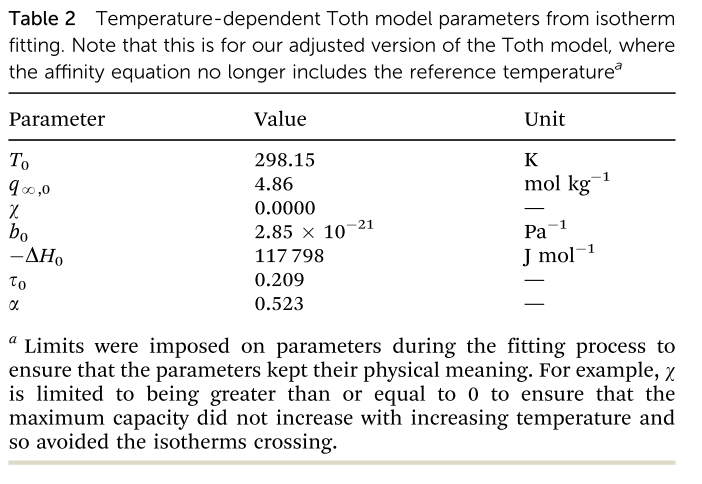
(1) At high water loadings, amine efficiency may be limited by hydrogen-bonded water structures blocking CO2 access to amine sites.

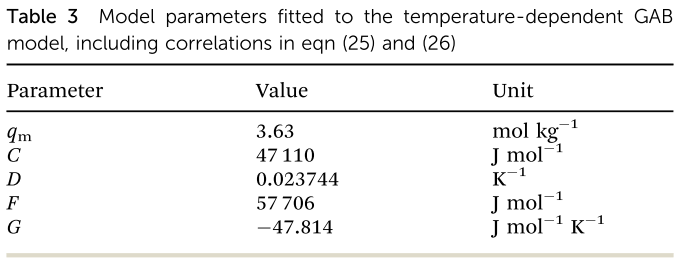
(2) The presence of water can increase the stoichiometric ratio due to ammonium bicarbonate forming rather than ammonium carbamate.

(3) The presence of water changes the heats of adsorption of adsorbed CO2 species hence the affinity

There are two possible models to describe the detailed chemistry at play on the surface of the adsorbent: a Mechanistic co-adsorption model: (MCM) and an empirical weighted-average dual-site Toth co-adsorption model (WADST). In this simulation, we use WADST only (see Young, J., García-Díez, E., Garcia, S. & van der Spek, M. “The impact of binary water–CO 2 isotherm models on the optimal performance of sorbent-based direct air capture processes”. Energy Environ. Sci. 14, 5377–5394 (2021)).

#### WADST Isotherm Model for CO2





#### Alterative Adsorption Isotherm Models

