Computational Analysis of Pre-Combustion CO_2 Capture via Pressure Swing Adsorption (PSA)

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Overview

- Introduction/ Motivation
- Research Context
- Aims and Objectives
- Methodology
- Results
- Future work

Introduction/ Motivation

- IPCC indicated that carbon capture (CCS) is a crucial technology to meet the 2°C target (iea-ghg,2017).
    - Climate scenarios show that the target cannot be met without CCS (COP21 and COP23)
    - Why? The costs of meeting the 2°C will be 138% higher if CCS is not included as a mitigation option
- There are large reserves of coal, estimated to be 200 years (BP, 2013)
- Coal power plants are responsible for the largest CO2 emissions (Global CCS institute, 2012)

https://www.iea.org/newsroom/energysnapshots/oecd-electricity-production-by-source-1974-2016.html

Introduction/ Motivation

- Main technologies for CCS…
    - Absorption
    - Cryogenic Distillation
    - Membrane Diffusion
    - Adsorption
- Adsorption…
    - Avoid issues, such as, corrosion and toxicity (Safety and Sustainability)
    - Higher energy efficiency values expected (Cost/ Sustainability)
    - Less water usage (Cost/ Sustainability)

Aaron, D.; Tsouris, C. Separation of CO_2 from Flue Gas: A Review. *Separation Science and Technology* **2005**, *40*(1-3), 321-348.

Research Context. Pressure Swing Adsorption (PSA)

- Definition: Dynamic process which operates at high pressure and low pressure in a fixed-bed reactor for cyclic adsorption and desorption
- Widely and confidently used for a range of gas separation processes
- Applications...
  - ○ Hydrogen purification
  - ○ Air separation (Nitrogen/ Oxygen enrichment)
  - ○ Ethanol dehydration
  - ○ Carbon Capture (future prospects)
- Design requires both material and process evaluation

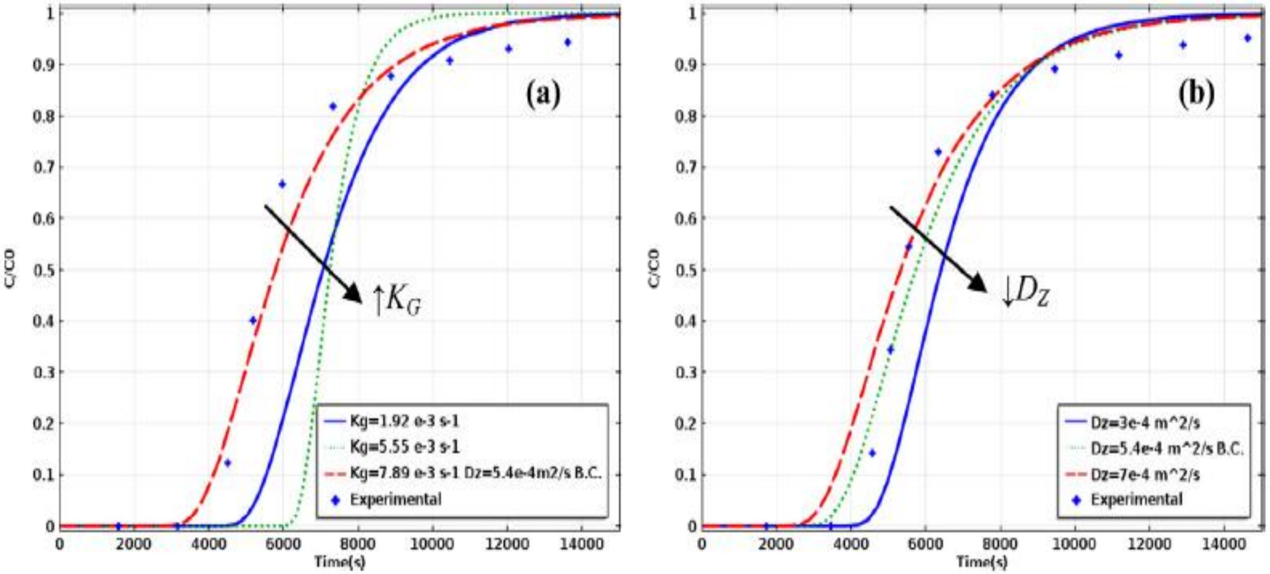
Research Context. Activated Carbons

- Activated carbons (AC’s) show higher capacity and selectivity when operating at high pressures (Pre-combustion)
- The increase on temperature can have a critical effect on the adsorption capacities of AC’s
- Neglectable effect of humidity on the adsorption capacity in pre-combustion conditions
- Modification of the adsorbents
  - At high pressures… the surface physical properties of the adsorbent become important rather than the chemical properties

Research Context. Effect on the Breakthrough Curves

- When validating a PSA model against experimental data, several studies have shown that the properties of the adsorbent and the mass transfer variables mainly influence the shape of the breakthrough curve

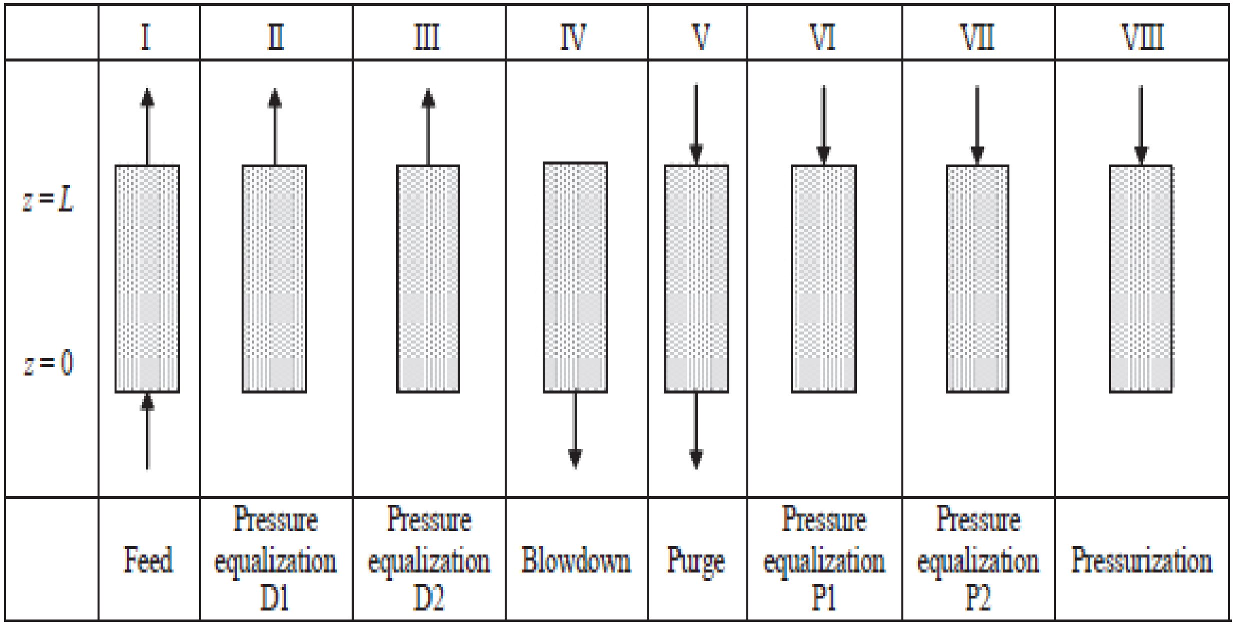
- Variables…
  - ○ Particle void fraction
  - ○ Particle diameter
  - ○ Bed void fraction
  - ○ Mass transfer coefficient
  - ○ Dispersion



Aguilera and Ortiz, 2016.

Research Context. Process Design

- Steps of PSA…
  - Pressurization
  - Adsorption
  - (Pressure equalization)
  - Blowdown
  - (Rinse)
  - Purge
  - (Pressure equalization)
  - (Null)



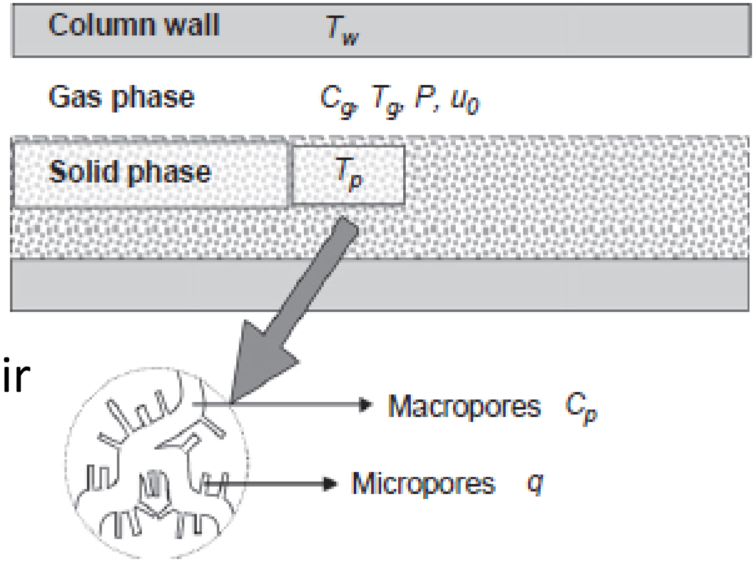
Ribeiro et al., 2008

Research Context. Process Design

- Challenges when designing PSA systems (PSE, 2017)
  - Selection of a suitable adsorbent and particle size
  - Selecting an isotherm model and parameters which represent the equilibrium data
  - Fixed-bed size for each pressure range
  - Determination of steps to be included and cycle time
  - Power requirements for the system
  - Capital and operating costs of adsorbent, vessels, power etc.
- Challenges of PSA operation
  - Pressure ratio selection between different steps
  - Extent of purge
  - Configuration of pressure equalization step

Research Context. Modelling PSA

- We need to consider…
  - Convective and dispersive flow
  - Adsorption (heat generation)
  - Bed to wall and wall to ambient heat transfer
  - Pressure drop (momentum losses)
  - Adsorption isotherm (Dual-site Langmuir isotherm)
  - Pressure and temperature dependent mass transfer coefficients
  - Linear Driving Force assumption (LDF)



Ribeiro et al., 2008

Research Context. Modelling PSA

- Mass, energy and momentum balances, as well as, mass/ energy transfer and isotherm equations are used to describe the PSA model

Mass Balance

$$\frac{dC}{dt} = -v\frac{dC}{dz} - \frac{1-\varepsilon}{\varepsilon}e\frac{dQ}{dt} + D_e\frac{d^2C}{dz^2}$$

Energy Balance

$$\left(\varepsilon\, e_g Cp_g + e_s Cp_s\right)\frac{dT}{dt} = -\varepsilon\, e_g Cp_g v\frac{dT}{dz} + e_s\sum_{i=1}^{n}\Delta H_i\frac{dQ_i}{dt} + U_A(T_n - T_w) + \alpha\frac{d^2C}{dz^2}$$

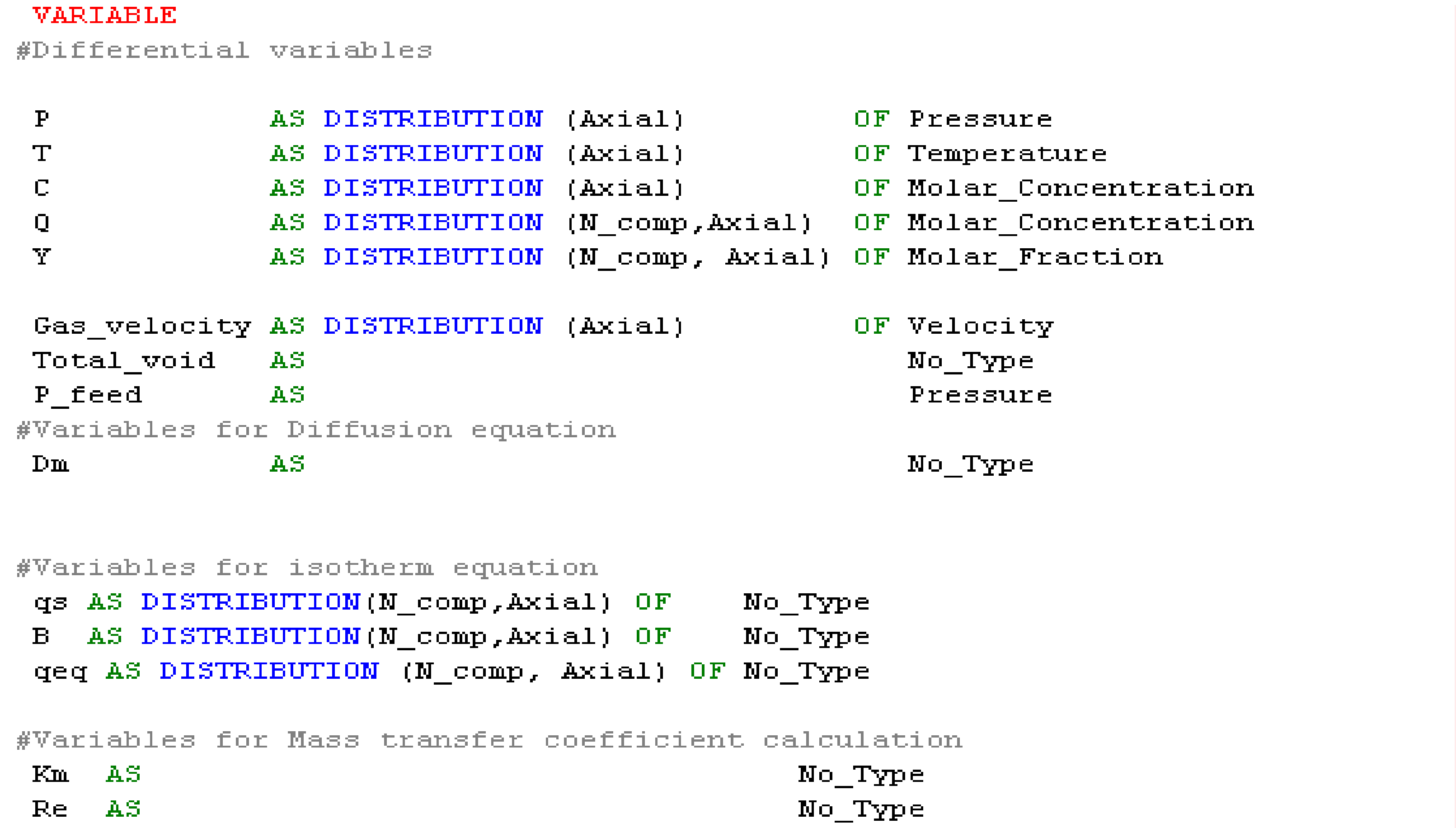
Dual-site Langmuir isotherm

$$Q^*_{(i,z)} = \frac{q^S_{1i}b_{1i}C_iRT(z)}{1+\sum_j b_{1j}C_jRT(z)} + \frac{q^S_{2i}b_{2i}C_iRT(z)}{1+\sum_j b_{2j}C_jRT(z)}$$

Aims and Objectives

- Find the steps for **PSA schedule**, which optimize the purity and recovery of CO_2 and H_2 products
  - Find the expressions in the adsorption process which give similar results compared to **laboratory data** (Mass/ heat transfer, dispersion…)
  - **Schedule the steps** with a fixed time, considering the optimum approaches to change the steps
  - Introduction of **new beds** which increase recovery/ purity of the products
  - **Optimization** of PSA schedule to maximize energy efficiency and product purity and recovery (timing, pressure…)
- Analysis of the **PSA performance in a IGCC power plant** (pre-combustion)
  - **Cost analysis** (Capital and operating costs)

Methodology



```
 VARIABLE
#Differential variables

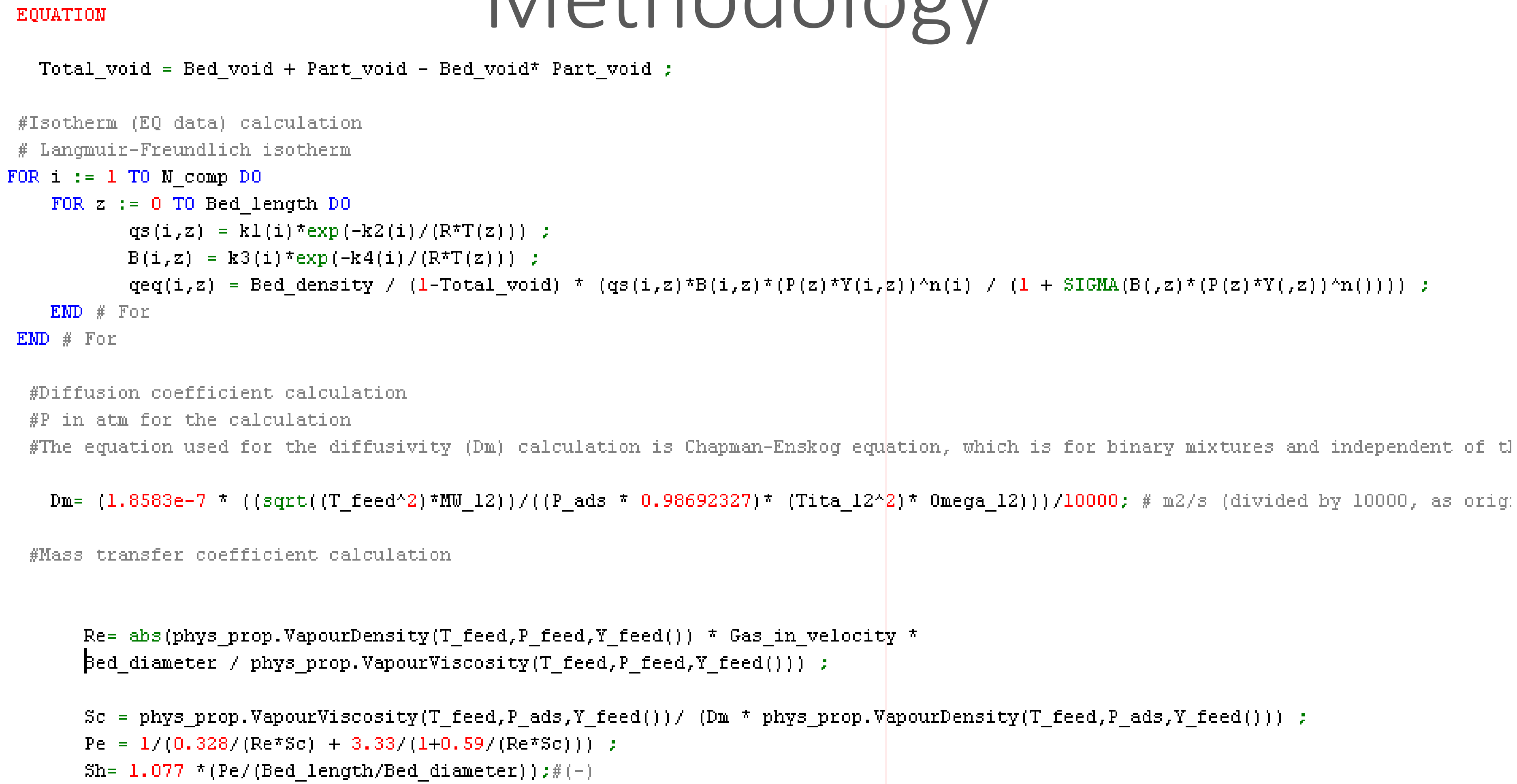
 P             AS DISTRIBUTION (Axial)          OF Pressure
 T             AS DISTRIBUTION (Axial)          OF Temperature
 C             AS DISTRIBUTION (Axial)          OF Molar_Concentration
 Q             AS DISTRIBUTION (N_comp,Axial)   OF Molar_Concentration
 Y             AS DISTRIBUTION (N_comp, Axial)  OF Molar_Fraction

 Gas_velocity  AS DISTRIBUTION (Axial)          OF Velocity
 Total_void    AS                                  No_Type
 P_feed        AS                                  Pressure
#Variables for Diffusion equation
 Dm            AS                                  No_Type


#Variables for isotherm equation
 qs  AS DISTRIBUTION(N_comp,Axial) OF     No_Type
 B   AS DISTRIBUTION(N_comp,Axial) OF     No_Type
 qeq AS DISTRIBUTION (N_comp, Axial) OF No_Type

#Variables for Mass transfer coefficient calculation
 Km   AS                                       No_Type
 Re   AS                                       No_Type
```

Methodology



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EQUATION

  Total_void = Bed_void + Part_void - Bed_void* Part_void ;

 #Isotherm (EQ data) calculation
 # Langmuir-Freundlich isotherm
FOR i := 1 TO N_comp DO
    FOR z := 0 TO Bed_length DO
           qs(i,z) = k1(i)*exp(-k2(i)/(R*T(z))) ;
           B(i,z) = k3(i)*exp(-k4(i)/(R*T(z))) ;
           qeq(i,z) = Bed_density / (1-Total_void) * (qs(i,z)*B(i,z)*(P(z)*Y(i,z))^n(i) / (1 + SIGMA(B(,z)*(P(z)*Y(,z))^n()))) ;
    END # For
 END # For

  #Diffusion coefficient calculation
  #P in atm for the calculation
  #The equation used for the diffusivity (Dm) calculation is Chapman-Enskog equation, which is for binary mixtures and independent of th

    Dm= (1.8583e-7 * ((sqrt((T_feed^2)*MW_12))/((P_ads * 0.98692327)* (Tita_12^2)* Omega_12)))/10000; # m2/s (divided by 10000, as orig

  #Mass transfer coefficient calculation

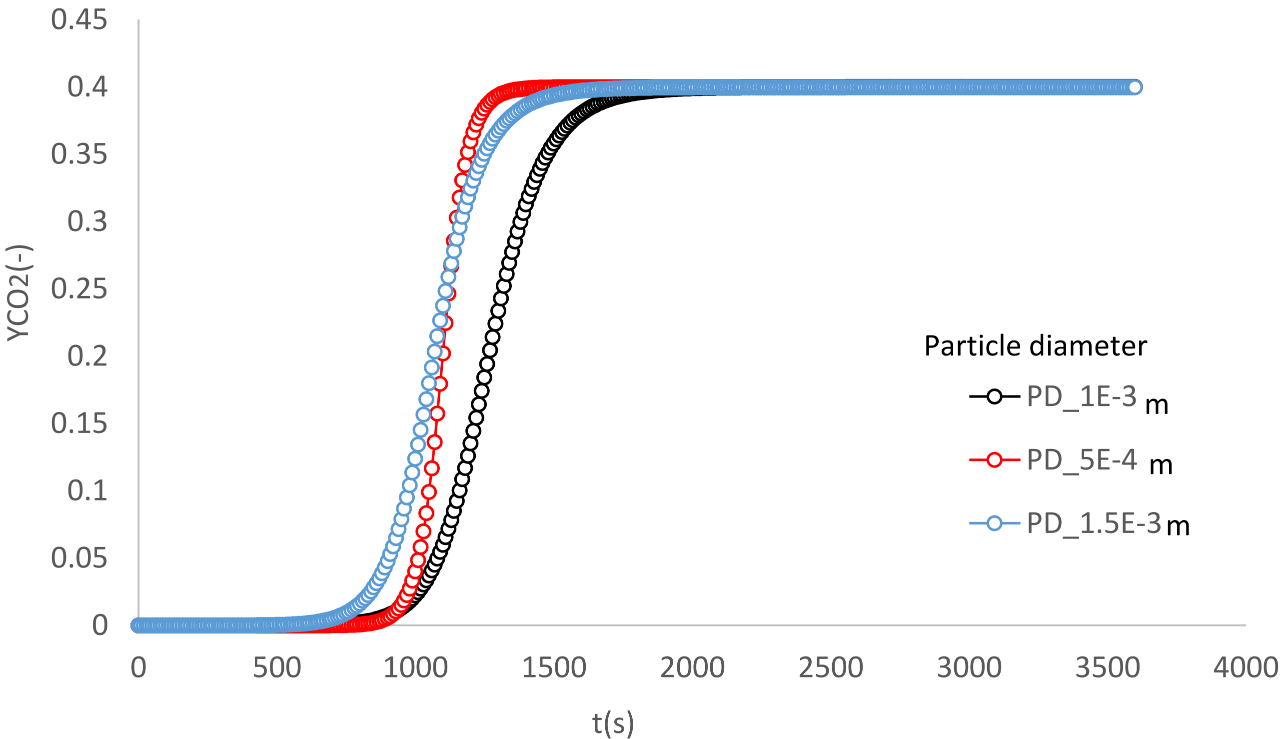

       Re= abs(phys_prop.VapourDensity(T_feed,P_feed,Y_feed()) * Gas_in_velocity *
       Bed_diameter / phys_prop.VapourViscosity(T_feed,P_feed,Y_feed())) ;

       Sc = phys_prop.VapourViscosity(T_feed,P_ads,Y_feed())/ (Dm * phys_prop.VapourDensity(T_feed,P_ads,Y_feed())) ;
       Pe = 1/(0.328/(Re*Sc) + 3.33/(1+0.59/(Re*Sc))) ;
       Sh= 1.077 *(Pe/(Bed_length/Bed_diameter));#(-)
```

Results

1. Validation of the feed step model

- **Sensitivity analysis** for the adsorbent properties
  - Particle diameter
  - Particle/ bed voidage fraction
  - Mass transfer coefficient
- Feed conditions
  - 40% CO_2
  - 60% H_2
- Particle diameter (PD) sensitivity analysis
  - Aim: check model robustness for **parameter estimation**



Results

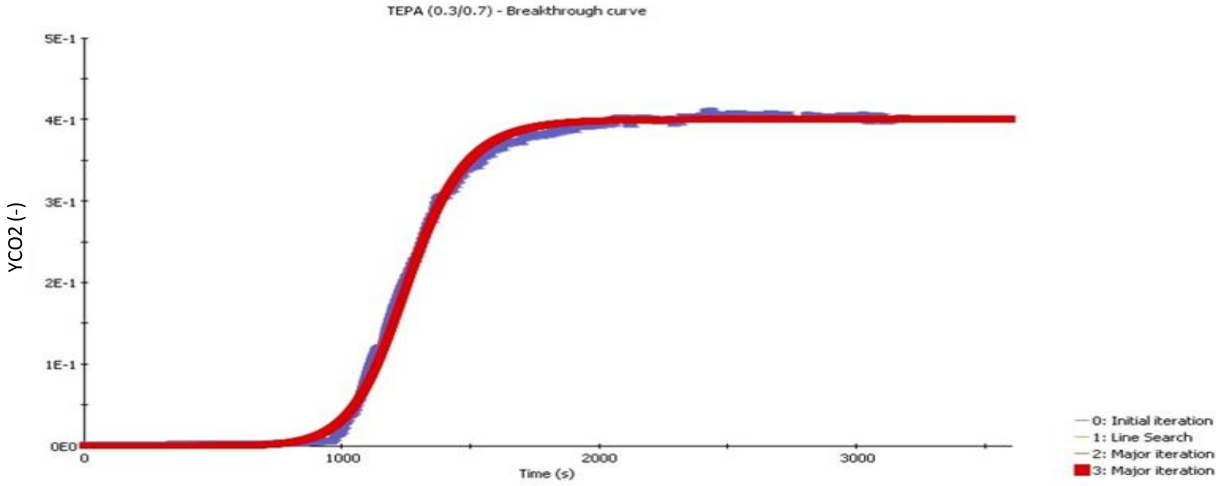
1. Validation of the feed step model

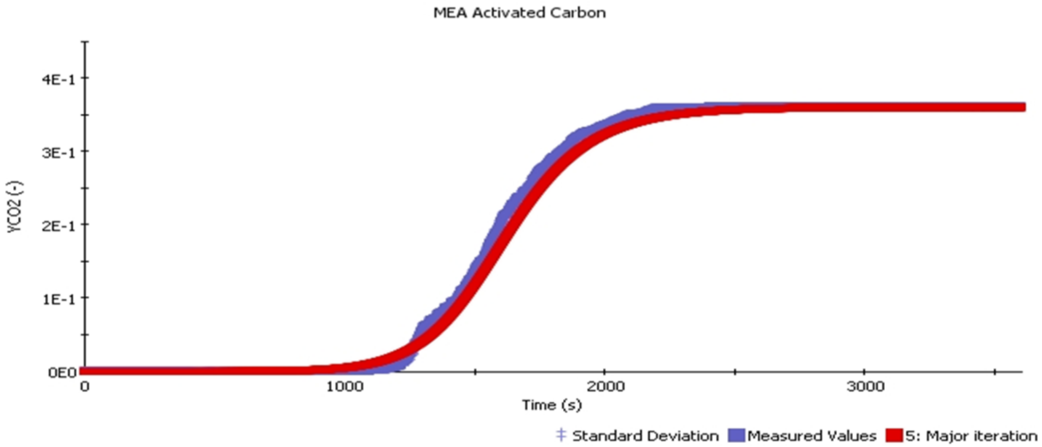
- Parameter estimation results with TEPA and MEA modified AC's.

- Feed conditions
  - ○ 40% CO_2
  - ○ 60% H_2
  - ○ T =298K

- Parameter estimation results

	SSR	Mass transfer coefficient (s^{-1})
KOH AC	6.2E-1	0.07
MEA AC	3.8E-1	0.025
TEPA AC	1.4E-1	0.04

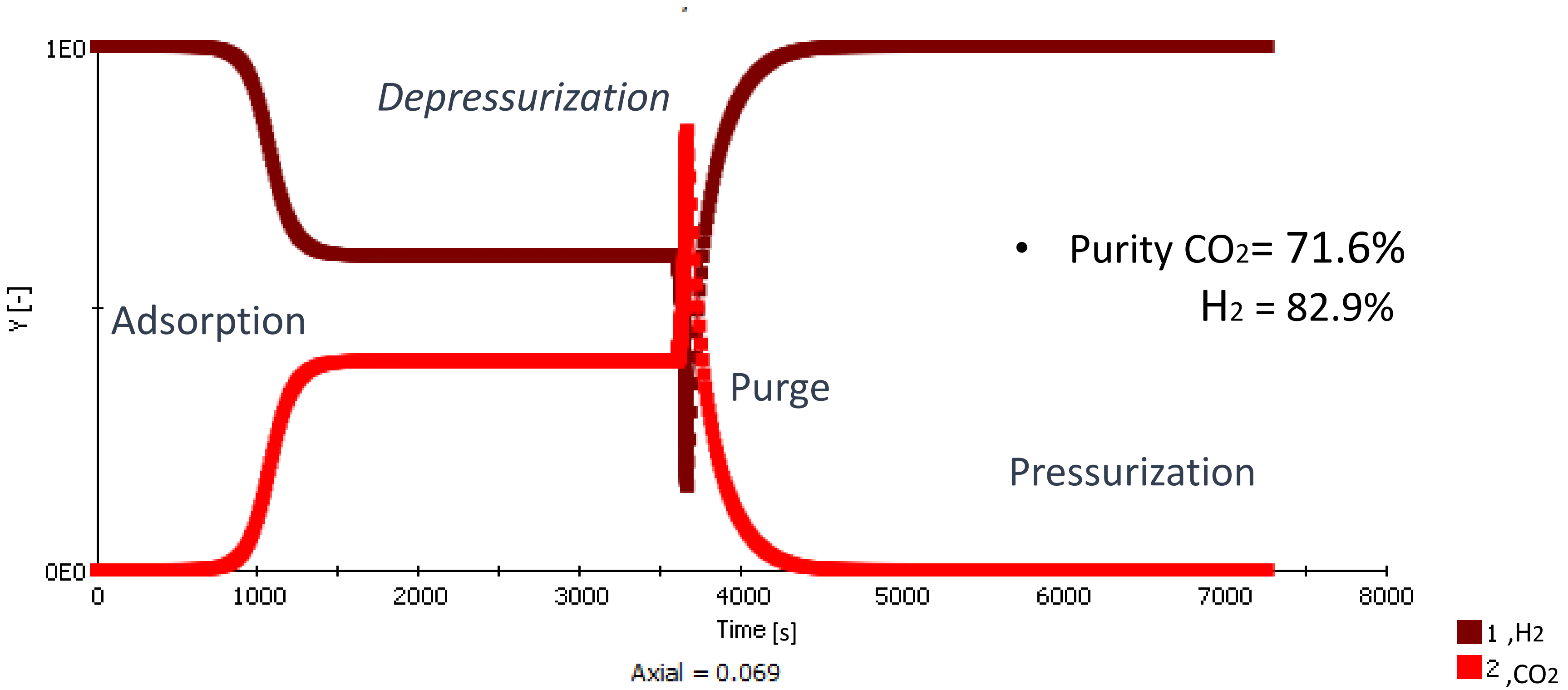

TEPA (0.3/0.7) - Breakthrough curve


MEA Activated Carbon

Results

2. Multiple step model

- 4- step PSA process

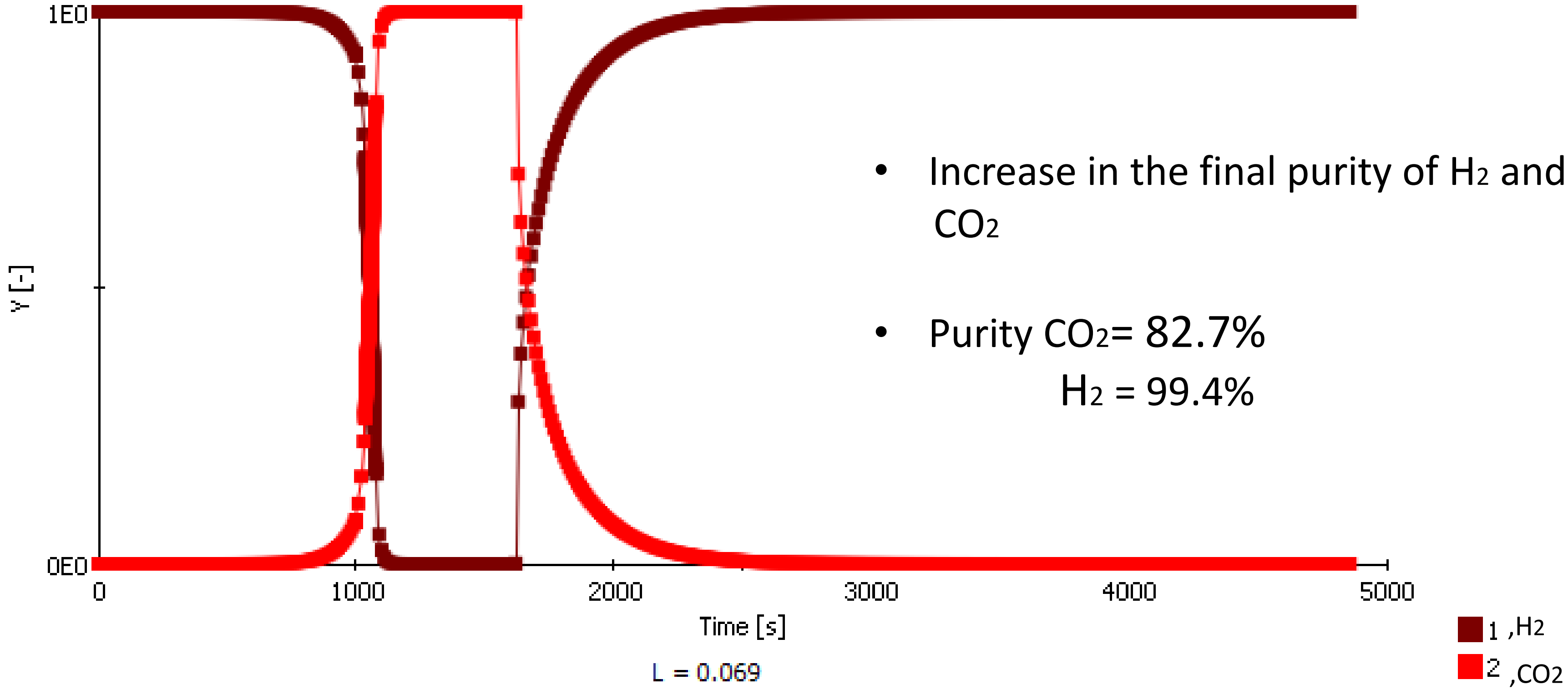


- Purity CO_2= 71.6%
  H_2 = 82.9%

Results

2. Multiple step model

- 6- step PSA process (Pressure equalization and Rinse included)



- Increase in the final purity of H_2 and CO_2
- Purity CO_2= 82.7%
  H_2 = 99.4%

Results

2. Multiple step model

- **Sensitivity analysis** for the six- step PSA process

Particle diameter (m)	Purity H_2/CO_2 (%)	Particle void fraction (-)	Purity H_2/CO_2 (%)
0.75×10^{-3}	99.5/82.1	0.55	99.4/82.7
1×10^{-3}*	99.4/81.9	0.74*	99.4/81.9
1.25×10^{-3}	99.3/81.6	0.85	99.4/81.6
Bed void fraction (-)	**Purity H_2/ CO_2 (%)**	**MT coefficient (s^{-1})**	**Purity H_2/ CO_2 (%)**
0.48*	99.4/81.9	0.02	99.2/71.9
0.6	99.4/81	0.04*	99.4/81.9
0.7	99.5/80.8	0.1	99.5/90.3

* Standard laboratory value

Results

2. Multiple step model

- **Sensitivity analysis** for the six- step PSA process

Feed pressure (Pa)	**Purity H_2/ CO_2 (%)**	**Purge pressure (Pa)**	**Purity H_2/ CO_2 (%)**
15×10^5	99.4/ 74.8	0.5×10^5	99.4/ 96.4
20×10^5	99.4/ 79.2	1×10^5*	99.4/ 81.9
25×10^5*	99.4/ 81.9	1.5×10^5	99.4/ 77
CO_2 feed fraction (mol CO_2/ total mol)	**Purity H_2/ CO_2 (%)**	**Reactor length/ diameter ratio (m/ m)**	**Purity H_2/ CO_2 (%)**
0.3	99.3/ 73	2.5	99.5/ 84.7
0.4*	99.4/ 81.9	2.76*	99.4/ 81.9
0.6	99.5/ 91.6	3.5	99.1/ 79.5

* Standard laboratory value

Future work

- Multiple- bed model of PSA
- Optimization of PSA schedule to maximize energy efficiency and product purity and recovery (timing, pressure…)
- Integration of PSA in an IGCC power plant (pre-combustion)
- Cost analysis (Capital and operating costs) of the plant

Conclusion

- A 4 and 6 step PSA model was developed, which included amine modified Norit® activated carbon properties from laboratory experiments.
- Parameter estimation was used for model validation against laboratory fixed bed reactor experiments.
- A sensitivity analysis carried out with adsorbent parameters and process variables showed that mass transfer properties, feed gas conditions and reactor size had the biggest influence in the final purity of the gas components.

Thank you for listening

Questions?

CDT in Carbon Capture and Storage and cleaner fossil energy