

# CO<sub>2</sub> Separation from Flue Gases by Adsorption

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This paper deals with gas separation by adsorption processes. The key objective is to investigate the adsorption suitability for Post-combustion Carbon Dioxide (CO<sub>2</sub>) Capture (PCC). Adsorption is a promising technology suitable for a high volume of diluted gas processing. Unlike commercialised amine-based absorption processes, adsorption seems to require less energy for sorbent regeneration and extends the sorbent lifetime. Two common industrial methods utilizing a difference in adsorption equilibrium of the gas components were investigated: 1) Pressure Swing Adsorption (PSA) including Vacuum Swing Adsorption (VSA), 2) Temperature Swing Adsorption (TSA). A comparison of their energy consumption, suitability for industrial use with consideration of Carbon Capture and Storage standards is evaluated. A complex mathematical model for the adsorption step of the fixed bed adsorber was proposed and solved by the structural programming. Three adsorbent materials: Mg-MOF-74, UTSA-16, and Zeolite 13X were evaluated based on their CO<sub>2</sub> adsorption capacity, selectivity, and market availability. Zeolite 13X was further explored. As a benchmark case, a medium-sized natural gas cogeneration unit was used to study the potential of VSA unit. The lower limit of CO<sub>2</sub> capture efficiency in simulations was 75 %. The results presented in this paper suggest that adsorption can be a feasible CO<sub>2</sub> capture solution for a low-carbon emission power generation technologies. Optimal parameters for the adsorption step and column configuration are proposed.

## 1. Introduction

CO<sub>2</sub> capture has become a topic of increasing interest over the last few decades as fossil and conventional fuels still represent a majority of energy supplies and global strategies towards cleaner environment such as green industrial policy are promoted throughout the European Union (Tagliapietra and Veugelers, 2020).

In general, there are several CO<sub>2</sub> capture technologies, e.g., absorption, adsorption, membrane separation, hydrates, cryogenic distillation, and combustion technologies, e.g., Oxy-fuel or Chemical Looping Combustion that are examined more-or-less in detail. Absorption is the most mature and widely explored capture technology, which is preferred for the PCC. A commercialised physical absorption processes are, e.g., Selexol, Rectisol and Purisol. The chemical absorption, a typical benchmark case, often employs amine-based processes, e.g., Monoethanolamine Solvents (MEA). Adsorption is attractive for its high adsorption capacity, long-term stability, low regeneration cost and low energy requirements. Still, a lot of effort is required to further investigate operating cost, capital cost, operability under non-laboratory conditions and adsorbents CO<sub>2</sub> capacity including resistance against impurities, which would provide better insight into industrial use in power plants (Sifat and Haseli, 2019). Retrofitting power plant requires PCC technology as a final gas treatment process due to technical challenges of Pre-combustion capture. The inlet flue gas is without impurities and carries typically 5 – 25 vol. % CO<sub>2</sub> depending on the fuel. Its temperature is approx. 293 – 313 K at around atmospheric pressure.

The comparison of MEA absorption, 4-step TSA using Activated Carbon (AC) and polymer membranes separation on a 20 MW Coal-Fired Power Plant for the PCC scenario, was studied by Anselmi et al. (2019) for CO<sub>2</sub> purity of 95 %, recovery of 75 % and production capacity of 1,000 kg<sub>CO2</sub>/h with the results favouring membrane separation. Jiang et al. (2019) investigated integration of 4-step TSA using AC into a 411 MW Natural Gas Combined Cycle Power Plant and approx. 800 MW subcritical sequential supplementary firing combined cycle for PCC. Energy, exergy and economic analysis suggested adsorption competitiveness to the MEA

absorption. A 4-step VSA cycle was analysed on the techno-economical basis by Subraveti et al. (2021) using simulation of a steam-methane reformer process. VSA cycle was evaluated for flue gas with 20 vol. % of CO<sub>2</sub> and compared to MEA absorption. A hybrid CO<sub>2</sub> capture system was optimised for a 300 MW Black Coal-Fired Power Plant with CO<sub>2</sub> emissions of 1.01 t/MWh and required only 17 % more energy than MEA absorption (Fong et al., 2016). Wawrzyńczak et al. (2019) used a 9-step dual-reflux VSA with layered AC to study CO<sub>2</sub> removal in 460 MW mobile pilot plant producing a flue gas with 13.8 % of CO<sub>2</sub>; however, outlined high energy demand of the vacuum pump reaching 978 kWh/t<sub>CO2</sub>. Additional summary can be found in the Subraveti et al. (2021). Adsorption system industrial potential for PCC was investigated by several authors. Most studies address process simulation and experiments on the lab-scale, e.g., effect of the column geometry, gas parameters and adsorbent material selection on the cycle performance. This work aims to analyse the possibilities of adsorption system utilisation in a medium-sized power system represented by industrial cogeneration unit (CGU). The focus was put on the conceptual design of VSA and its key process parameters for the CGU. The presented paper is the first part of a broader project of techno-economical evaluation of PCC from medium-sized emission point source.

## 2. Methodology

In the adsorption process design for CO<sub>2</sub> capture, there are two main types: PSA and TSA processes. Both processes are based on a physical adsorption and high selectivity of CO<sub>2</sub> molecules in the presence of N<sub>2</sub>. PSA is based on the dependence of adsorbed amount of gas on pressure. Pressure swings to the atmospheric pressure are used to regenerate the adsorbent while the heavy component is adsorbed at high pressures. TSA is a temperature alternating process. Desorption by heating is significantly longer such that fast cycling is possible only in pressure alternating cycles. If the desorption operates at lower than atmospheric pressures close to vacuum, cycle is referred to as VSA. VSA cycles are more suited for PCC in systems with high flow rates as PSA requires auxiliary compression unit to pressurise the flue gas. There have been some attempts to increase CO<sub>2</sub> capture efficiency by combining characteristics of PSA and TSA into a single unit, i.e., pressure and thermal swing adsorption (coupling) cycle. The overall performance of coupling cycles indicated some promises; however, the complexity of the design and process control do not allow a large-scale application at this point (Dhoke et al., 2021).

Comparison of the above-mentioned cycles for PCC by Plaza et al. (2010) showed insufficient productivity of TSA due to shorter cycle times (40 %) and low PCC efficiency but using vacuum during desorption significantly improved process performance. VSA becomes superior to TSA for PCC in overall aspects. The energy consumption of VSA cycles is determined by the vacuum level (over 70 %). Desorption by vacuum makes adsorption technology competitive to the commercially available MEA absorption, which is energy intensive and the regeneration of corrosive amine solvents less effective. The main drawbacks of VSA units include a large area footprint, a need of gas pre-treatment, presence of impurities in the flue gas, high pressure drops that, in summation, limit large-scale integration (Chao et al., 2021).

### 2.1 Adsorption isotherms

Adsorption isotherms assess separation process feasibility, suggest operating pressure range per cycle, and adsorbent material characteristics. A suitable adsorbent possesses good selectivity between the separated impurities and remaining components in the gas mixture, high impurities uptake, working capacity and regenerability. The “heavy” component should be adsorbed substantially faster, stronger and in higher amounts than the “light” components. Physical adsorbents for CO<sub>2</sub> capture were reviewed in detail by many authors (e.g., Abd et al., 2020). Modak and Jana (2019) analysed their progress towards PCC. Based on those reviews, AC was excluded due to insufficient adsorption capacity and lower selectivity towards CO<sub>2</sub>, despite its low price and good market availability. Three adsorbents: Zeolite 13X, Metal–Organic Frameworks (MOFs) UTSA-16 and Mg-MOF-74 were compared. The adsorption equilibrium of these adsorbents for CO<sub>2</sub>-N<sub>2</sub> is represented by Competitive dual-site Langmuir model (DSL) (Rajagopalan et al., 2016):

$$q_i^* = \frac{q_{sb,i} b_i c_i}{1 + \sum_{i=1}^{n_{comp}} b_i c_i} + \frac{q_{sd,i} d_i c_i}{1 + \sum_{i=1}^{n_{comp}} d_i c_i} \quad (1)$$

The adsorption isotherms were plotted for the temperature of 313 K and CO<sub>2</sub> partial pressure 0 – 15 vol. %, see Figure 1. Mg-MOF-74 possessed the highest adsorption capacity. Further research showed lack of industrial application and limited market availability at high price (Subraveti et al., 2021). UTSA-16 showed low and linear CO<sub>2</sub> adsorption capacity. Zeolite 13X was selected as the significantly higher adsorbed amount of CO<sub>2</sub> over N<sub>2</sub> confirms good selectivity and suitability for PCC.

The flue gas produced by combustion also contains water vapour and O<sub>2</sub> (combustion with excess air). While O<sub>2</sub> does not affect the equilibrium, the presence of water vapour is problematic. Water vapour affects the shape

of adsorption isotherm and tends to condense, which leads to adsorbent degradation and material surface damage (Yang and Xiang, 2019). separation of water vapour before the adsorption process is essential.

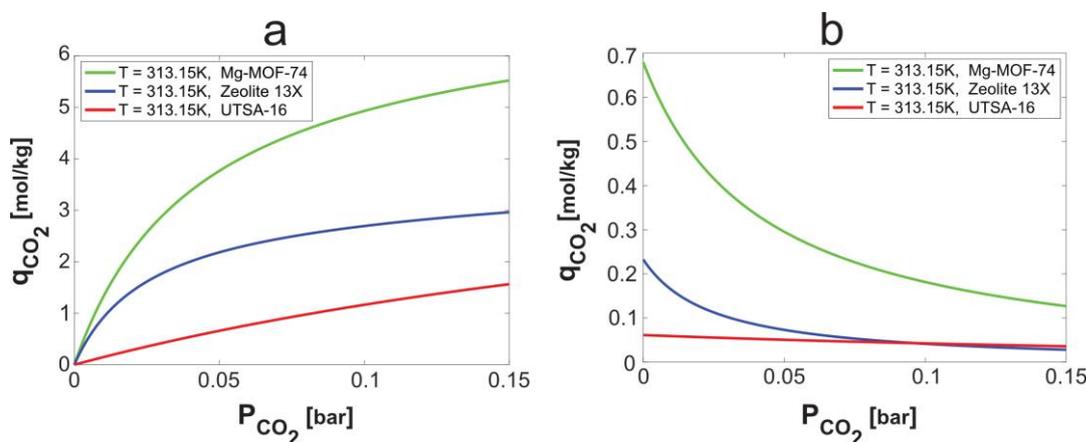


Figure 1. Adsorption equilibria of the binary mixture on the investigated adsorbents (a)  $CO_2$ , (b)  $N_2$ .

## 2.2 Process description

A medium-sized emission source (3 m x 3 m x 15 m - height x width x length), Natural Gas-Fired CGU TEDOM Quanto D200, with the nominal electric power of 2 MW and thermal output of 2.3 MW was considered. These units serve as a local power supply of industrial facilities or at the city districts level. The volumetric flow of flue gas emitted is 9,000  $Sm^3/h$ . To meet 75 vol. %  $CO_2$  capture efficiency, a single stage concept with 8-bed VSA unit was proposed. After combustion, the flue gas is cooled and dehumidified. At the temperature of 313 K, pressure of 1 atm and composition: 84 vol. %  $N_2$ , 10 vol. %  $O_2$  and 6 vol. %  $CO_2$ , the flue gas enters the VSA unit. Number of four fixed-bed column pairs was chosen to split the high flue gas flow rate. Each column is packed with pelletised Zeolite 13X. To prevent high-pressure drops, 2 mm pellets were used. A conceptual process flow diagram of the system is in the Figure 2.

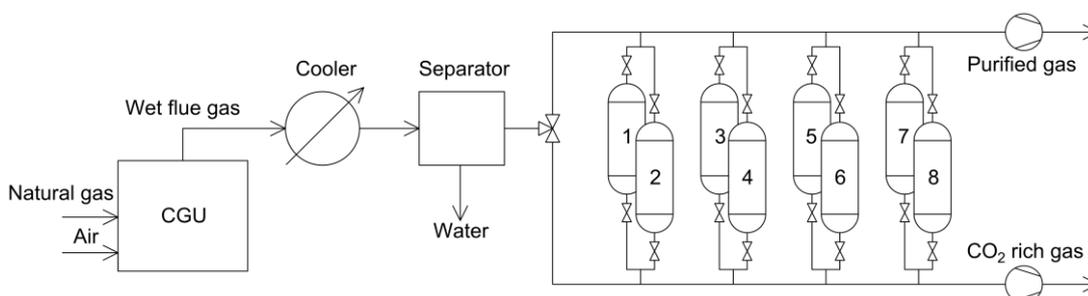


Figure 2. Conceptual process flow diagram of VSA PCC for a medium size emission source.

Figure 2 does not show the detail of pipeline branches and valves, but the process philosophy. The length-to-diameter ratio of 2 with the column diameter 1 m was used. A large build-up area of the system compensates partly for high pressure drops of long reactors. The bed void fraction of 0.4 was assumed. The superficial gas velocity of 0.75 m/s and the interstitial velocity of 1.9 m/s were calculated. For the adsorbent bulk density of 640  $kg/m^3$ , the weight of the column packing is approx. 1 t.

Scheduling of the VSA is based on one-bed VSA cycle with 4 steps. 1. Pressurisation: the column, which was initially at vacuum, is pressurised to an atmospheric pressure ( $P_A$ ) by the feed while the product end of the column is closed. 2. Adsorption: the product end is open, and the column is co-currently fed. The  $CO_2$  is adsorbed while the purified gas leaves the column. 3. Forward Blowdown: the feed end is closed; the column is depressurised to an intermediate pressure ( $P_I$ ) from the product end to remove the residual  $N_2$  from the column. The  $CO_2$  remains in the column as an adsorbate. 4. Reverse Evacuation: counter-current evacuation to a low pressure ( $P_L$ ) from the feed end to recover the adsorbed  $CO_2$  at high purity.

To achieve a better performance, the VSA cycle was modified by a well-established Skarstrom Cycle and extended by Light Product Purging and Pressurisation. Such modification requires bed pairing and consists of 6 steps. The paired beds run in opposite steps. When the Bed 2 is pressurised to  $P_A$ , the Bed 1 is evacuated to

$P_L$ . After that, the Bed 2 starts the adsorption step, and the light product is used to purge the CO<sub>2</sub> from the Bed 1. Next step is a modified Forward Blowdown: Bed 2 feed end and Bed 1 product end are closed. The pressure of beds is equalised to  $P_I$ . This step reduces the energy consumption of vacuum pumps and improves product recovery. Next three steps are reversed. The step arrangement of paired columns and the pressure history of one cycle are shown in Figure 3.

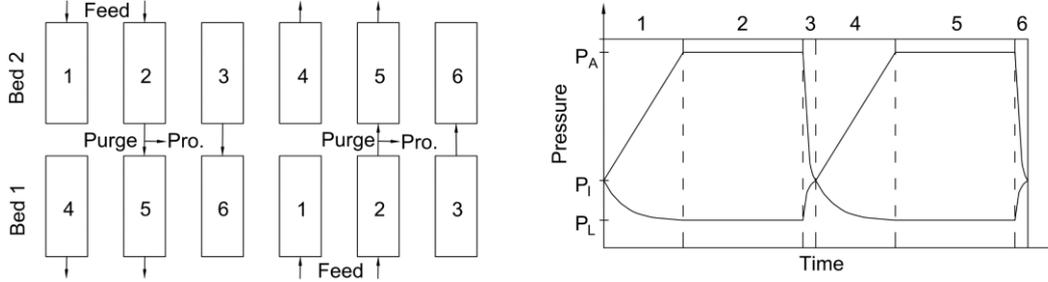


Figure 3. Step arrangement and pressure history of both columns during proposed VSA cycle.

The steps timing presented in Figure 3 is indicative and the industrial data-based optimisation by the parametric programming will be the topic of further research (the effect of feed, e.g., gas physical properties, volumetric flow, desorption pressure, pre-pressurisation, number of columns and geometry of the system on the breakthrough time). It should be noted that one pair does not provide continuous process, but the proposed four pair setup allows it. The performance of the VSA strongly depends on  $P_L$ , which affects CO<sub>2</sub> purity and total energy consumption. Vacuum pressure of 13 kPa is recommended based on the industrial practices, where the pump cannot typically provide lower pressures. CO<sub>2</sub> capture efficiency was calculated to 75 %. Extending the VSA unit by a 2<sup>nd</sup> stage could increase capture efficiency up to 95 - 99 %.

### 2.3 Modelling

In this work, 1D axially dispersed plug-flow model without any changes of gas concentration in the radial axis, which is acceptable for the adsorbent-to-particle diameter over 10 (Gutiérrez Ortiz et al., 2019), is presented. The mathematical model simulates adsorption step of VSA cycle with a bulk separation of a binary gas mixture of N<sub>2</sub> and CO<sub>2</sub>. Process parameters are defined in the process description. Pelletised adsorbents typically cause wide adsorption waves (Dhoke et al., 2021); the effect of axial dispersion to predict the concentration curve more accurately is considered. Following assumptions were made: 1. The mass transfer rate is approximated by the Linear Driving Force (LDF) model. 2. Adsorption step is isothermal (negligible thermal effects caused by the adsorption heat). 3. There are no radial concentration or thermal gradients along the columns. 4. Gas phase parameters: viscosity, molar heat capacity and thermal conductivity are constant. 5. Gas phase is described by the Ideal Gas Law. 6. Axial fluid velocity and axial dispersion coefficient are constant along the column. 7. Pressure drop is expressed by the Ergun equation. Based on those assumptions, the gas phase mass balance for component  $i$  in the axial direction is following:

$$\frac{\partial c_i}{\partial t} = D_{ax} \frac{\partial^2 c_i}{\partial z^2} - v \frac{\partial c_i}{\partial z} - \rho_m \cdot \left( \frac{1-\varepsilon_b}{\varepsilon_b} \right) \frac{\partial q_i}{\partial t}, \quad \text{where} \quad \frac{\partial q_i}{\partial t} = k_{LDFi} \cdot (q_i^* - q_i). \quad (2)$$

with initial condition  $c_i(t = 0, \forall z) = 0$ . Dirichlet-type boundary condition for the gas phase concentration  $c_i$  at column inlet:  $c_i(\forall t, z = 0) = (P_0 \cdot y_{feed}) / (R_g \cdot T_0)$ , where index "0" refers to an inlet feed gas parameter, was used. The concentration of components in the gas phase does not change at column outlet, because no adsorption occurs. A Neumann-type boundary condition was defined as  $\frac{\partial c_i(\forall t, z=L)}{\partial z} = 0$ . A mass balance in the adsorbed phase, i.e., the source term:  $\partial q_i / \partial t$ , is simplified to the LDF model for particles with homogeneous structure, which describes the mass transfer resistance between the gas and solid phase. Fully regenerated adsorbent is assumed before the adsorption step starts:  $q_i(t = 0, \forall z) = 0$ . The equilibrium concentration  $q_i^*$  is expressed by the DSL model Eq(1). The diffusion flux in the macropores is defined by the combination of Knudsen and molecular diffusivity in the transient region ( $0.01 < Kn < 10$ ) (Roušar and Dittl, 1993). The axial dispersion coefficient was estimated according to Ruthven (1984). This estimation does not account for wall-channelling, which results in significant error only when the pellet-to-bed diameter is small (Son et al., 2018). The mass balances in gas and solid phase Eq(2) defines a system of Non-Linear Partial Differential Equations (PDEs). A Finite-Volume scheme was used to discretise the PDEs into the Ordinary Differential Equations, which are solved explicitly by the MATLAB (version 2021a, MathWorks, Natick, MA) stiff ODE solver, ode23s,

using modified Rosenbrock time integration method. The convective flux was discretised by the 1<sup>st</sup> order upwind scheme, which is oscillation free, but decreases the breakthrough estimation accuracy.

### 3. Results and Discussion

The mathematical simulation allowed to observe the course of the adsorption step and study the potential of the proposed VSA unit. The mass transfer is assessed by considering the LDF lumped coefficient  $k_{LDF_i}$  accounting for the macropore resistance as the main rate controlling mechanisms. Its value was modified by the slope of adsorption isotherm  $dq_i/dc_i$  resulting in a dynamic change of the mass transfer resistance over time.

Three dimensionless criteria – Biot number, Phi1 and Phi2 were calculated to analyse the breakthrough curve. The detailed definition of these criteria is in Roušar and Dittl (1986). Biot number > 10 confirmed that transport by diffusion is significant. The Phi1 factor accounts for the intraparticle diffusion effect on the breakthrough curve. The value of Phi1 < 1 was obtained for both components suggesting significant intraparticle diffusion. For Phi2 < 10<sup>-3</sup> the convection flux is dominant over axial dispersion, which can be neglected; however, for the computed value of Phi2 = 0.0028, the axial dispersion is included. The results from the mathematical model are presented in the Figure 4 of CO<sub>2</sub> breakthrough curve for different positions in the column. Three curves show that the breakthrough time changes almost linearly with the column length. This information can be used for process design and cycle step timing.

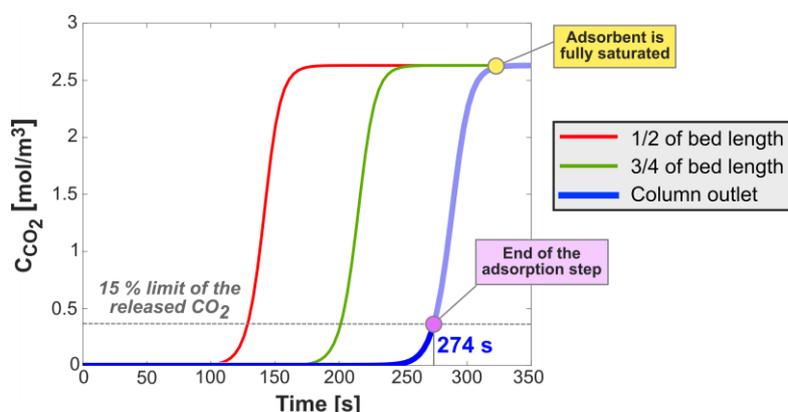


Figure 4. CO<sub>2</sub> breakthrough curve analysis for different positions in the column.

Obtained results were verified by the mass balance of the adsorption step duration. The end of adsorption step is defined by the CO<sub>2</sub> concentration of approx. 1 vol. % at the column outlet, i.e., the breakthrough curve ends at 15 vol. % of CO<sub>2</sub> inlet concentration. Such assumption increased the efficiency of adsorption per step and reduced the amount of unused adsorbent at the column outlet.

It should be noted that during different sets of simulations at constant flow rate, a significant dependence of the LDF lumped coefficient and the axial dispersion coefficient on the shape of the breakthrough curve were observed. In combination, these parameters indicate the slope of the mass transfer gradient between the gas and solid phase defining the breakthrough curve width (result of axial mixing). This fact is known, but a more detailed analysis considering high flowrates and large industrial columns as well as higher CO<sub>2</sub> amount in the flue gas, i.e., a Coal-Fired, Cement or Steel Power Plant would be an interesting topic for further studies.

### 4. Conclusions

In this work, results of a brief review focused on state-of-art PCC on an industrial scale by alternative methods to absorption are presented. Based on the review, a 6-step VSA is proposed, aiming at medium scale industrial CGU processing 9,000 Sm<sup>3</sup>/h of flue gas with 6 vol. % CO<sub>2</sub> with minimum CO<sub>2</sub> capture efficiency of at least 75 %. The proposed cycle includes Light Product Pressurisation, which leads to energy savings (vacuum pump work reduction) and higher product purity. The VSA unit consists of four pairs, i.e., 8 fixed-bed reactors with 1 m diameter and length of 2 m. Zeolite 13X was chosen from the theoretical comparison of several physical adsorbents. Its suitability was demonstrated with adsorption capacity analysis at operating CO<sub>2</sub> partial pressure range by the DSL model. A non-linear mathematical model of the adsorption step was also presented. The obtained results showed that the time of the adsorption step (defined by the appearance of 15 vol. % of CO<sub>2</sub> inlet amount at the column outlet) is 274 s. Model parameters were verified by inspection analysis using three criteria. Further work will focus on proposing piping and instrumentation diagram followed by optimising VSA cycle timing by more detailed modelling and techno-economic evaluation.

## Nomenclature

$b$ – Adsorption equilibrium parameter, [mol/m]	$\rho_m$ – adsorbent density [kg/m <sup>3</sup> ]
$c$ – Gas phase concentration, [mol/m <sup>3</sup> ]	$q$ – concentration in the solid phase, [mol/kg]
$D_{ax}$ – Axial dispersion coefficient, [m <sup>2</sup> /s]	$q_{sb}$ – saturation concentration for site1, [mol/kg]
$\varepsilon_b$ – bed void fraction, [-]	$q_{sd}$ – saturation concentration for site2, [mol/kg]
$k_{LDF}$ – LDF coefficient [1/s]	$v$ – Interstitial velocity, [m/s]
$n_{comp}$ – number of components in the mixture, [-]	

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