KSCT Fall Meeting

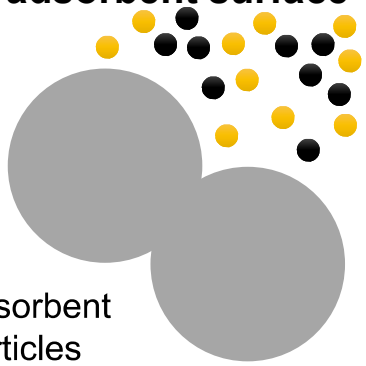
Theoretical Separation Feasibility of Zeolites for Gas Sweetening Process

Sep 9th
2021

Seongbin Ga
Pusan National University

How Adsorption Processes Work

Adsorption phenomena on adsorbent surface

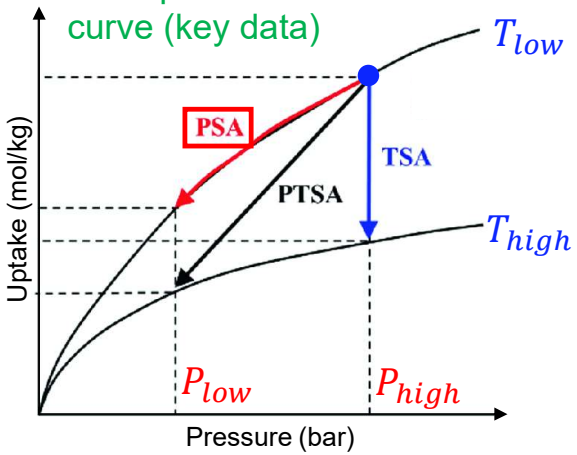


Adsorbent particles

Adsorption at condition 1:
High pressure (P_{high}),
Low temperature (T_{low})

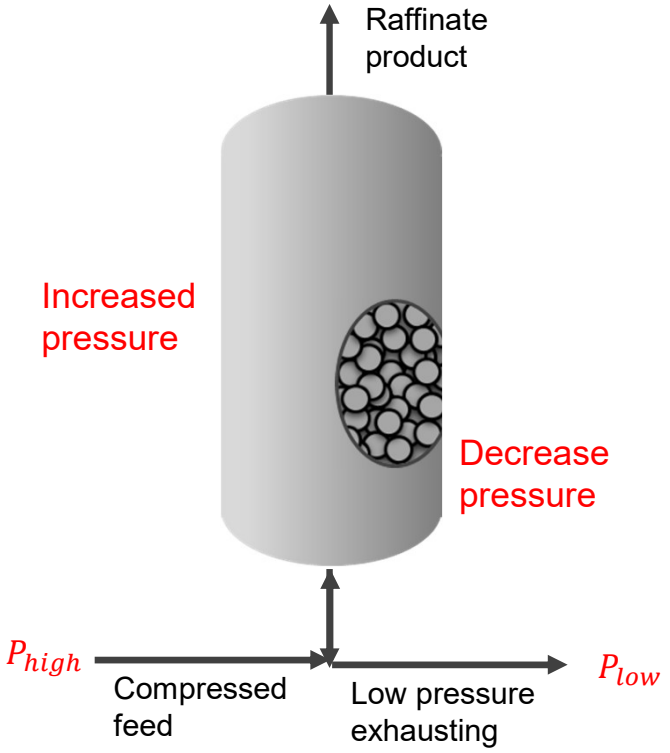
Desorption at condition 2:
Low pressure (P_{low}),
High temperature (T_{high})

Adsorption isotherm curve (key data)



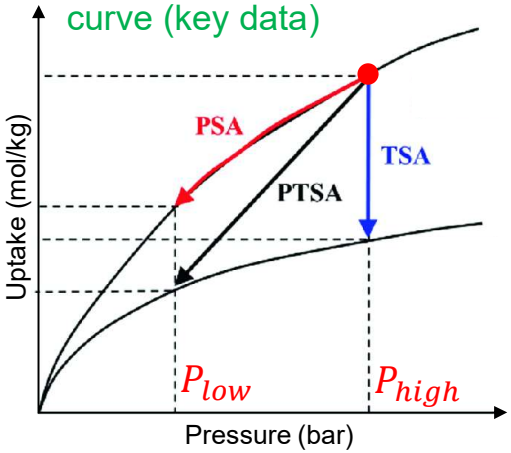
Pressures swing adsorption (PSA) process

Temperature swing adsorption (TSA) process



Cyclic Operation of Adsorption Process

Adsorption isotherm curve (key data)



Cyclic Operation of Adsorption Process

Cycle configuration

time (sec)

Step 1: adsorption

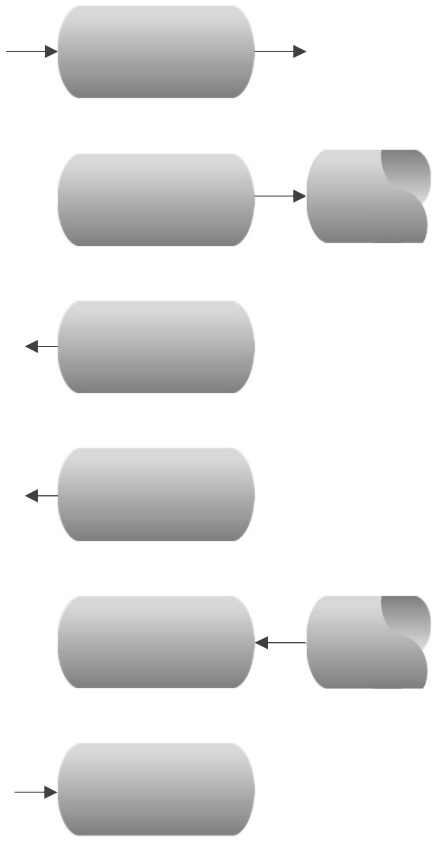
Step 2: pressure equalization (P↓)

Step 3: blowdown

Step 4: evacuation

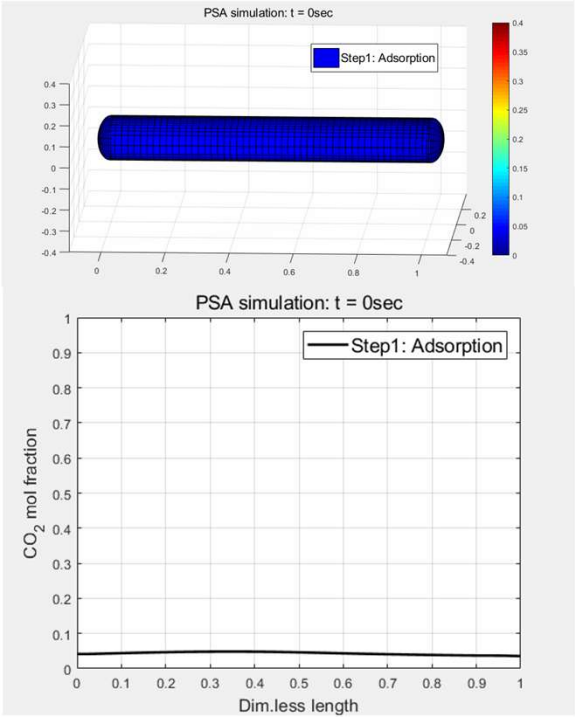
Step 5: pressure equalization (P↑)

Step 6: re-pressurization



Simulation results

e.g. CO_2/N_2 separation (gas phase concentration)



Process-level performance

Efficiency (CO_2 ton/ GJ)

$$\eta = \frac{M_{CO_2}}{E_{comp}}$$

CO_2 purity (mol/mol)

$$x = \frac{F_{CO_{2,ex}}}{F_{CO_{2,ex}} + F_{N_2,ex}}$$

Problem 1: CPU time

Suppose we have
many adsorbents to evaluate.

For each adsorbent, we need

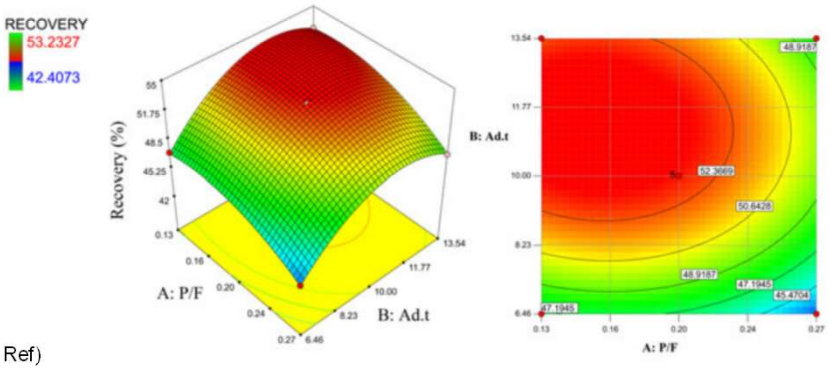
1) Dynamic simulations (min-level)
2) Cyclic steady state search (hr-level)
3) Design & operation optimization (day-level)

Operation optimization example

Adsorbent 1
→ optimal operation set 1

≠

Adsorbent 2
→ optimal operation set 2



Ref)
Saberimoghaddam, & Khebri, J. Chemometrics, 2016

Mass, momentum, and energy balance equations

Energy balance $$\frac{\partial T}{\partial t} = \frac{1}{\epsilon\rho_g c_g + (1-\epsilon)\rho_s c_s}\left((1-\epsilon)\rho_s \sum_i^2 (-\Delta H_i)\frac{\partial q_i}{\partial t} + \lambda_{ax}\frac{\partial^2 T}{\partial z^2} - \rho_g c_g u\frac{\partial T}{\partial z} - \rho_g c_g T\frac{\partial u}{\partial z} - \frac{2h_i}{r_{b,i}}(T - T_w)\right)$$

Overall mass balance $$\epsilon\frac{\partial C}{\partial t} + (1-\epsilon)\,\rho_s \sum_i^2 \frac{\partial q_i}{\partial t} + \epsilon u\frac{\partial C}{\partial z} + \epsilon C\frac{\partial u}{\partial z} = 0$$

Component mass balance $$\frac{\partial y_1}{\partial t} = -\frac{1-\epsilon}{C\epsilon}\rho_s\frac{\partial q_1}{\partial t} + \frac{D_{ax}}{C}\left(C\frac{\partial^2 y}{\partial z^2} + 2\frac{\partial C}{\partial z}\frac{\partial y_1}{\partial z} + y_1\frac{\partial^2 C}{\partial z^2}\right) - u\frac{\partial y_1}{\partial z} + \frac{y_1}{C}\frac{(1-\epsilon)}{\epsilon}\rho_s\sum_i^2\frac{\partial q_i}{\partial t}$$

Momentum balance $$-\frac{\partial P}{\partial z} = \frac{150.0(1-\epsilon)^2}{\epsilon^3}\frac{\mu}{d_p^2}u + 1.75 \times \frac{10^{-4}(1-\epsilon)}{\epsilon^3}\frac{\rho_g}{d_p}u|u|$$

Other assumed equations

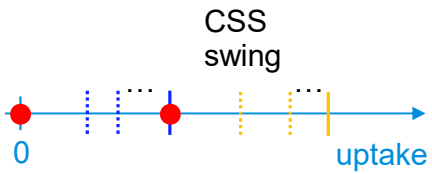
LDF model: $\frac{\partial q_i}{\partial t} = k_i(q_i^* - q_i)\ \ for\ i = 1,2$

Ideal gas equation: $PV = nRT$

Cyclic steady state (CSS) conditions

$for\ all\ i$
$for\ all\ \theta: all\ state\ variables$

$$\frac{\left(\theta_{z_i}|_{t=t_0}\right)_{(n)\text{th cycle}} - \left(\theta_{z_i}|_{t=t_f}\right)_{(n)\text{th cycle}}}{\left(\theta_{z_i}|_{t=t_0}\right)_{(n)\text{th cycle}}} < tolerance$$



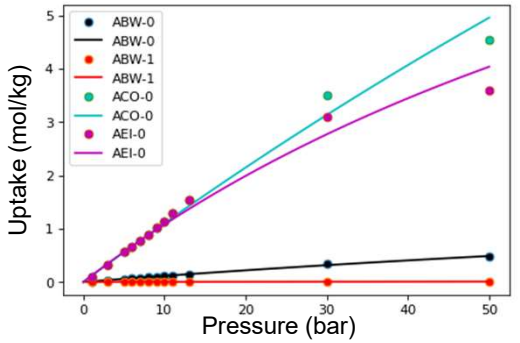
Problem 2: Limited information

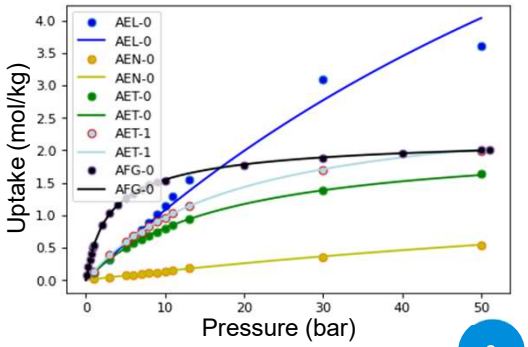
For the dynamic simulation for the PSA process,
a variety of adsorbent properties are essential:

Adsorption isotherm data, heat of adsorption,
mass/heat transfer coefficients, heat capacity, density ….

Most of them are rarely available,
especially when they are:
- newly discovered or
- newly developed or
- newly synthesized

Adsorption isotherm curves
= The first property they can obtain.





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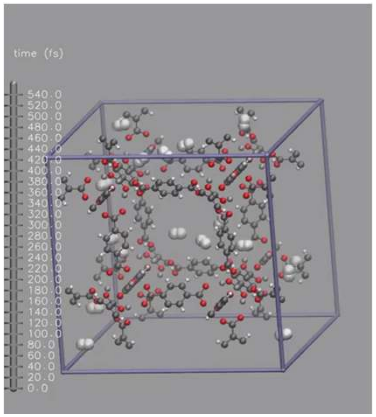
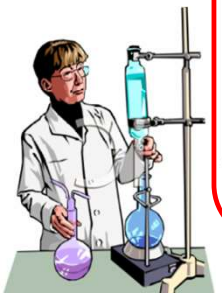
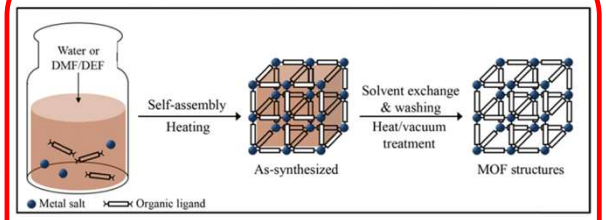
Molecular simulations



Synthesis of adsorbents



Various materials



Ref) Lee, Kim, and Ahn, *KJChE*, 2013

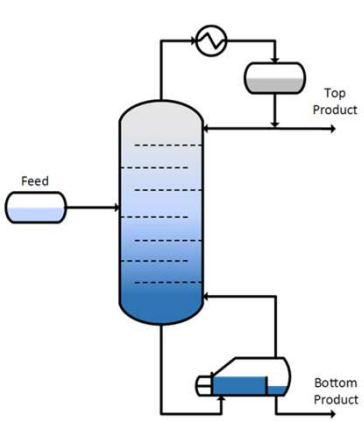
Idea: Ideal PSA Process

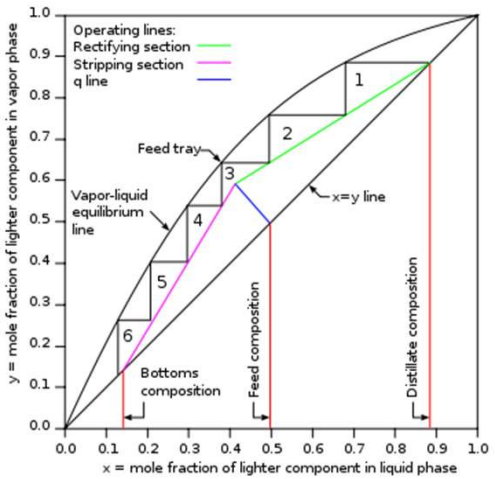
Inspired by McCabe Thiele method or Fenske equation

For distillation column

Equilibrium info.
Feed conditions
Target purity

→ Required process (operation or design)



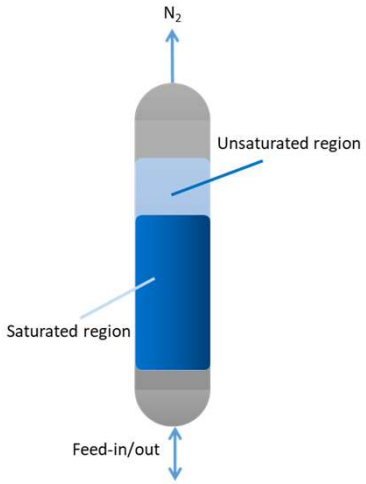


[**Shortcut method**: ideal PSA process]

For pressure swing adsorption (PSA) column

Isotherm info.
(Usually measured first)
Feed conditions
Target purity

→ Required process (operation or design)



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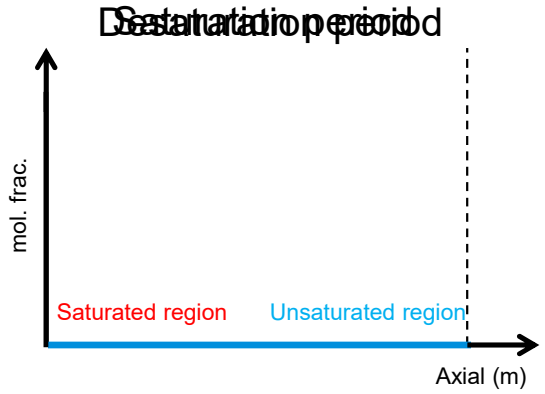
(Available for material developers)

Idea: Ideal PSA Process

[Shortcut method: ideal PSA process]

Derivation of the method (formula) starts from a set of assumptions (idealization):

- Two gas components
- No dispersion: clear saturated region boundary
- Two periods: saturation & desaturation
- Full capacity of the adsorbents
- Always in solid/gas equilibrium
- No effect of void volume



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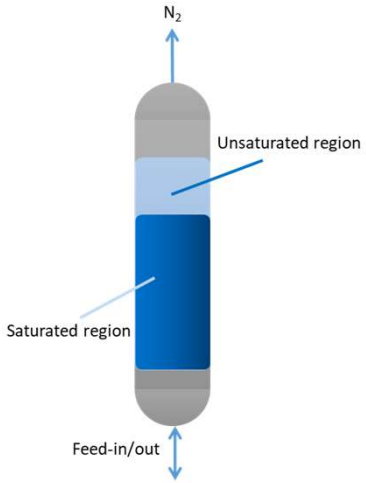


?

(Available for material developers)

Formula: Ideal PSA Process

New shortcut evaluation method

Efficiency

$$\eta = \frac{(\gamma-1)y_{flue}}{\gamma RT\left[\left(\frac{P_{high}}{P_{flue}}\right)^{\frac{\gamma-1}{\gamma}}-1\right]}$$

Purity

$$P_{high} = \frac{P_{low}}{(1+\bar{b}(x)P_{low})R_q - \bar{b}(y_{flue})P_{low}}$$

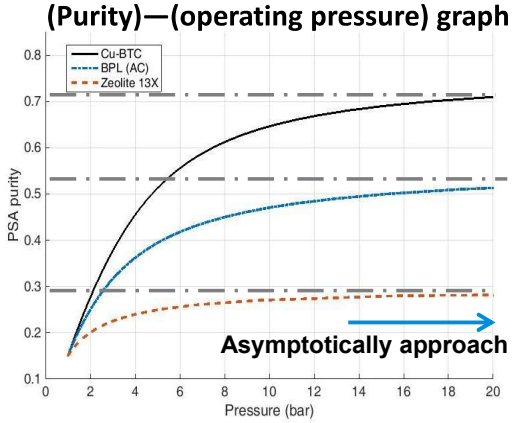
where

$$R_q = \frac{q_{m,1}b_1(1-x)y_{flue} - q_{m,2}b_2(1-y_{flue})}{x(1-x)(q_{m,1}b_1 - q_{m,2}b_2)}$$

$$\bar{b}(y_{flue}) = (b_1 - b_2)y_{flue} + b_2$$

$$\bar{b}(x) = (b_1 - b_2)x + b_2$$

(Purity)—(operating pressure) graph



$$\lim_{P\to\infty} x = ?$$

[Converges to a certain value]

$$Find\ x$$
$$such\ that\ P_{high} \to \infty$$
$$(denominator) \to +0$$

Advantages of them:

- Reflective of the application to the PSA process
- Easy to use and requiring only isotherm parameters
- Small computational cost
  (compared to PSA simulation time:
  ~2000 sec with successive substitution)

Upper limit of purity (purity cannot exceed this)

$$x_{upper} = \frac{-B - \sqrt{B^2 - 4AC}}{2A}$$

where

$$A = (q_{m,1} - q_{m,2})b_1b_2P_{low}$$

$$B = q_{m,1}(\beta_1 - b_1y_{flue}) + q_{m,2}\{\beta_2 - b_2(1-y_{flue})\}$$

$$C = (1+b_2P_{low})q_{m,1}b_1y_{flue}$$

$$\beta_1 = \{b_1(b_1-b_2) + b_1\bar{b}(y_{flue}) - b_1b_2y_{flue})P_{low}$$

$$\beta_2 = -\{b_2^2 + b_2\bar{b}(y_{flue})\}P_{low}$$

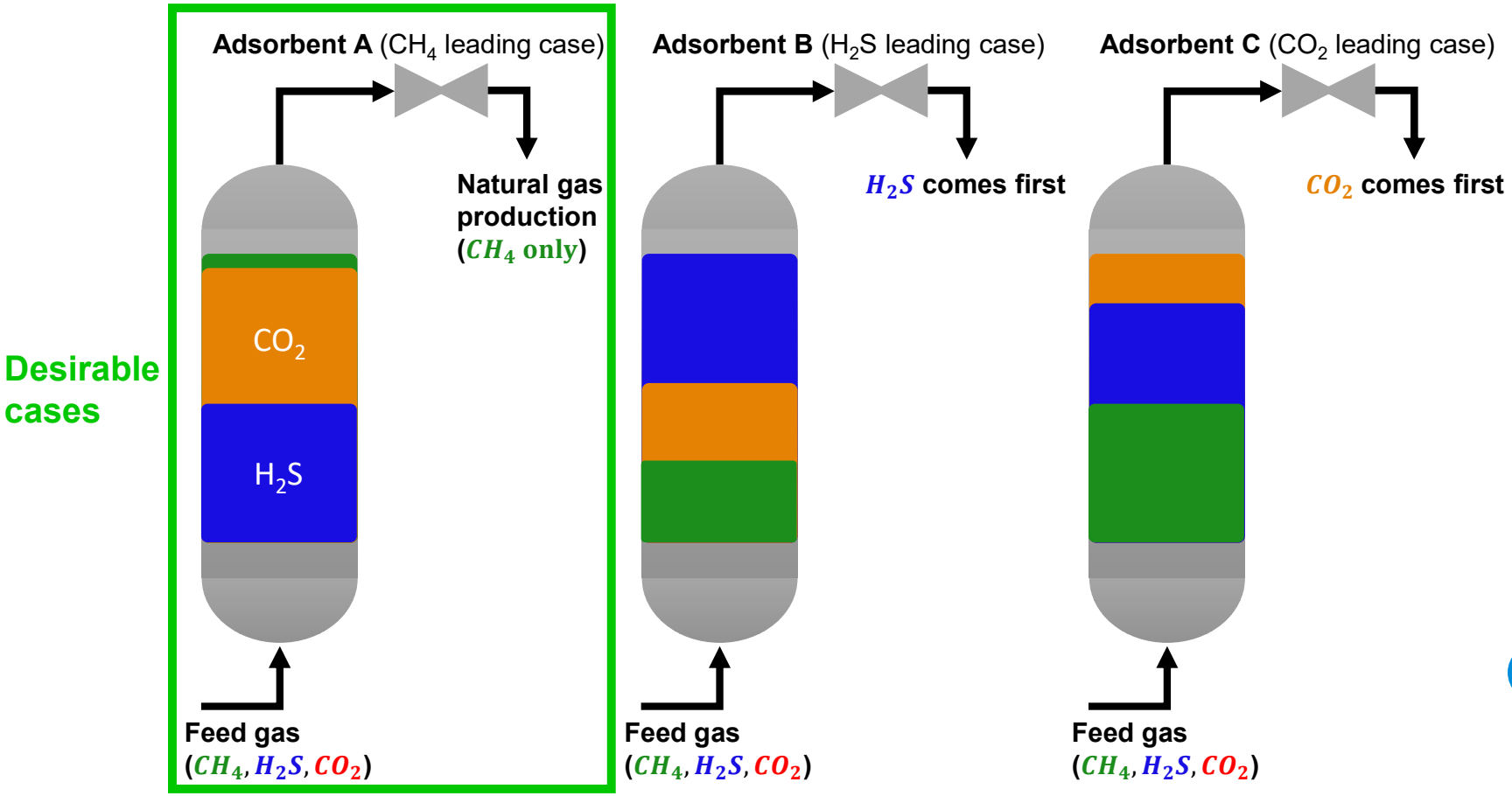
Proposed in

S. Ga et al., *Comput. Chem. Eng.*, 2017

Multi-component Case: $CH_4/H_2S/CO_2$

Natural gas sweetening process (feed gas contains $CH_4/H_2S/CO_2$):

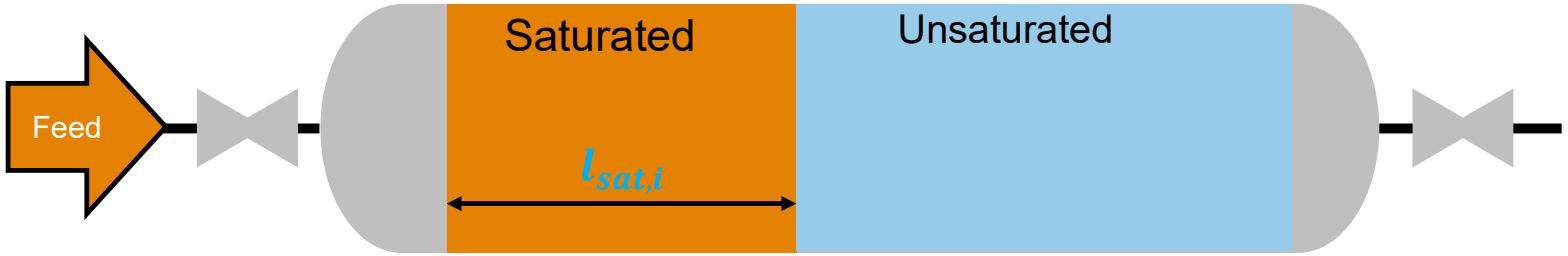
Different adsorbents can be classified into **three cases**.



Expansion Set of The Ideal PSA Method

Leading component concept

- During the adsorption step, the saturated region is propagated by the feed gas.
- The rate of saturation differs for each gas component.
- From the ideal PSA concept, we can calculate the rate of saturation as:



Rate of the saturation for component i (r_i)

$$r_i = \frac{l_{sat,i}}{\Delta t}$$

[Definition]

From the mass balance,

$$y_{in,i} F_{in} \Delta t = \rho_s (1-\varepsilon) A \, l_{sat,i} \Delta q_i$$

$$l_{sat,i} = \frac{y_{in,i} F_{in} \Delta t}{\rho_s (1-\varepsilon) A \Delta q_i}$$

[Length of saturation region]

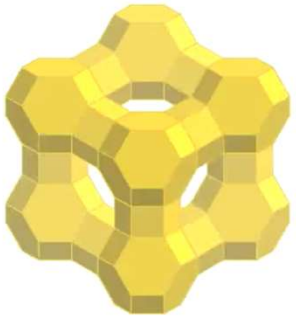
Therefore,

$$r_{CH_4} : r_{H_2S} : r_{CO_2} = \frac{y_{in,CH_4}}{\Delta q_{CH_4}} : \frac{y_{in,H_2S}}{\Delta q_{H_2S}} : \frac{y_{in,CO_2}}{\Delta q_{CO_2}}$$

[Ratio of the rate] = [Ratio of length]

Application to Zeolite Database

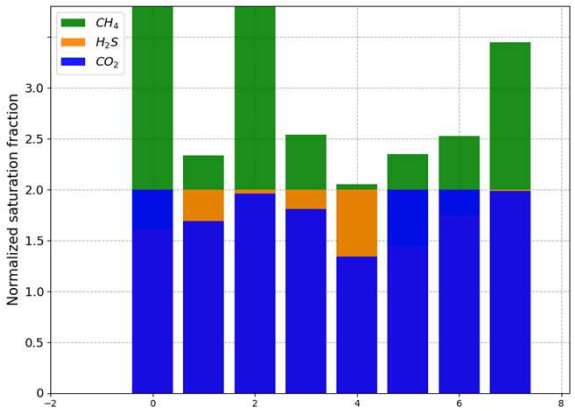
International Zeolite Association (IZA) database



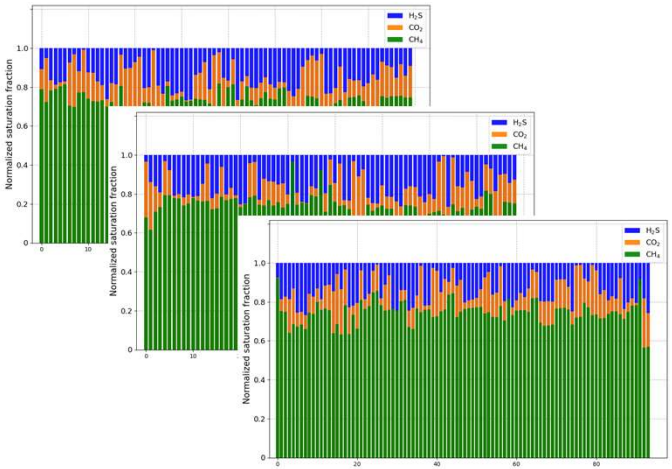
- Database providing structural information of over 300 zeolites
- Data in the crystallographic information framework (*.cif) file
- Online available database

Ideal PSA simulation Results: Classifying zeolites of IZA database

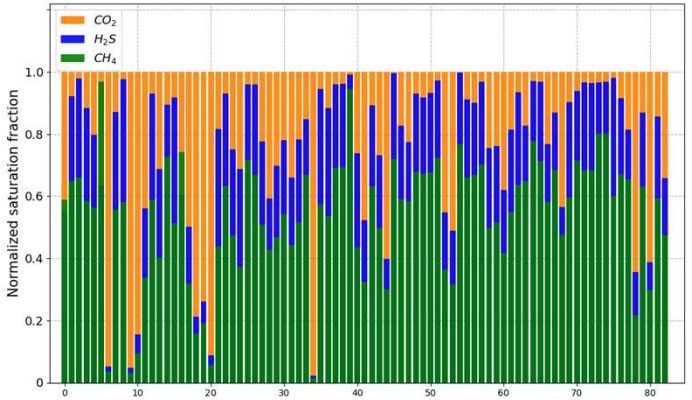
(1) CH_4 leading case (8 zeolites)



(2) H_2S leading case (255 zeolites)

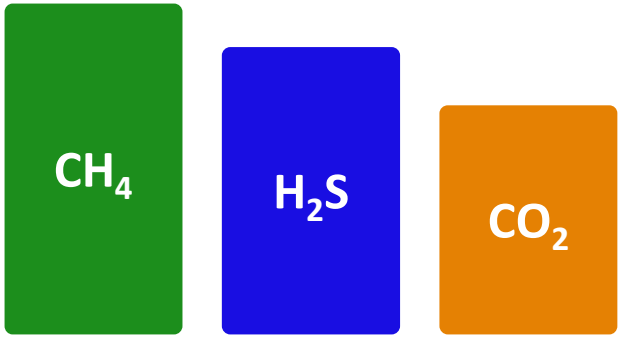


(3) CO_2 leading case (83 zeolites)



Visualization for Classification

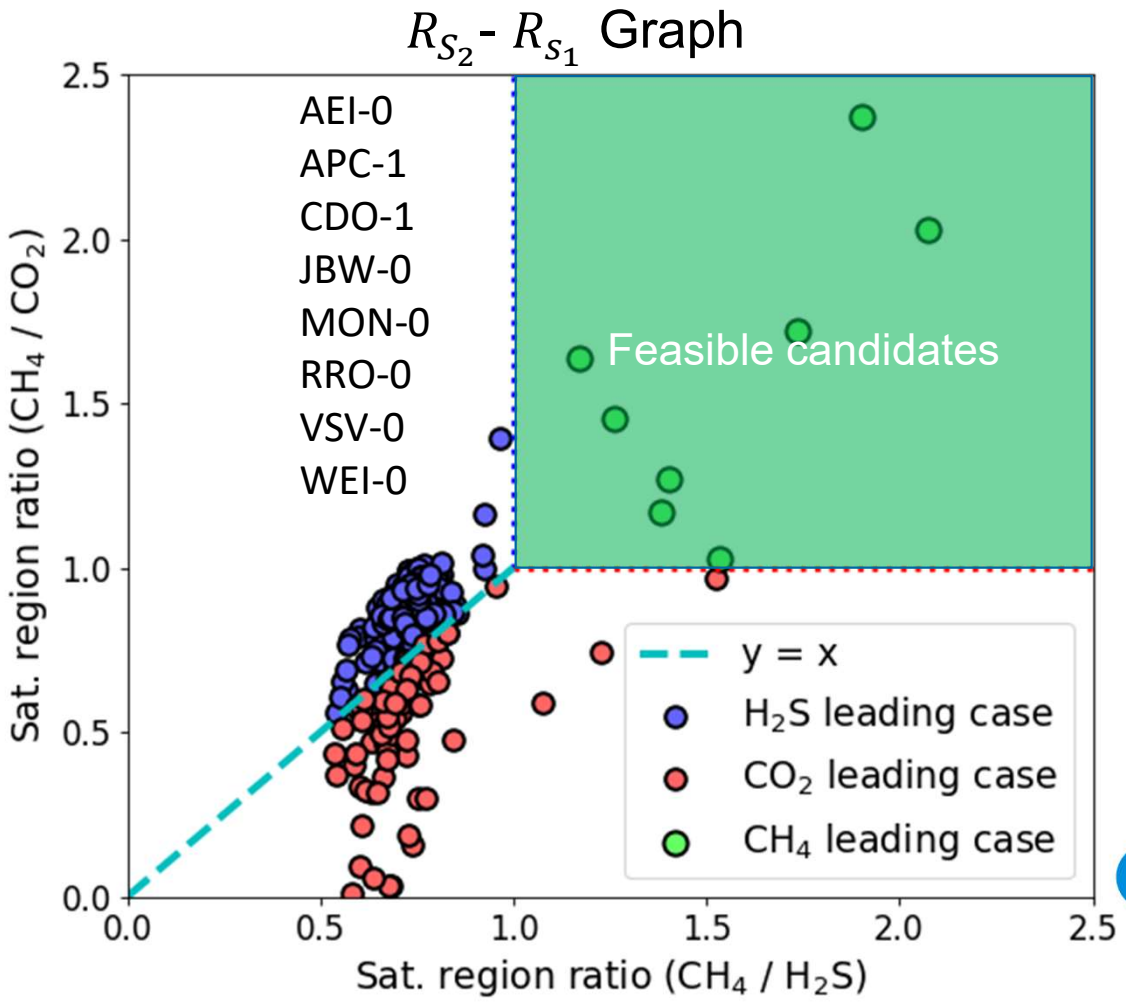
Different Saturation regions



Saturation region ratio

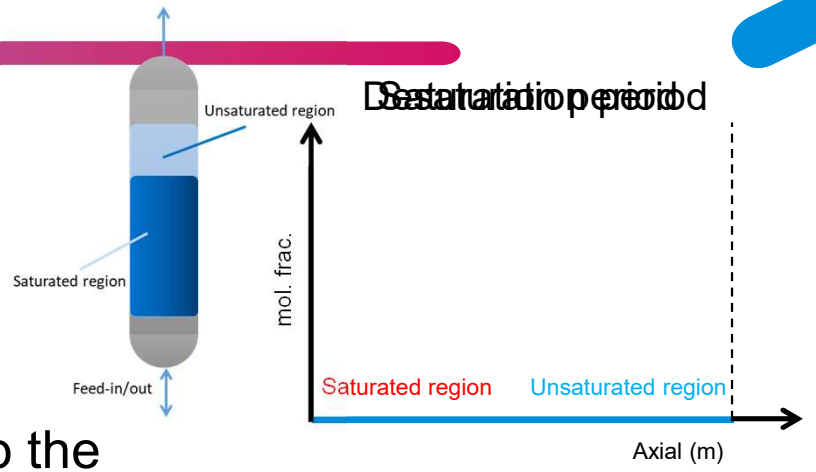
$$R_{s1} = \frac{CH_4}{H_2S} > 1$$

$$R_{s2} = \frac{CH_4}{CO_2} > 1$$



Conclusion

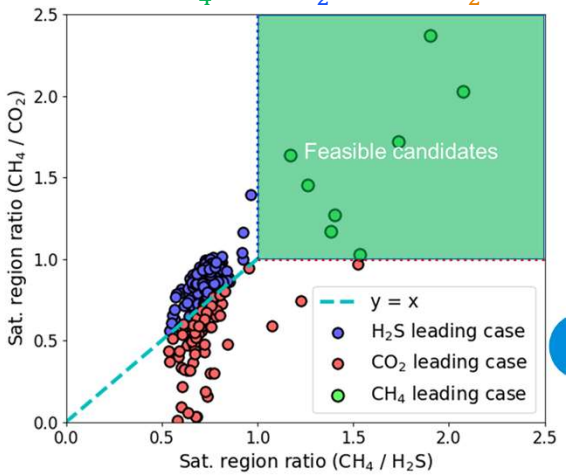
- Based on an ideal PSA process, shortcut evaluation method has been developed.



- The ideal PSA shortcut method is extended to the multi component gas separation system.

$$r_{CH_4} : r_{H_2S} : r_{CO_2} = \frac{y_{in,CH_4}}{\Delta q_{CH_4}} : \frac{y_{in,H_2S}}{\Delta q_{H_2S}} : \frac{y_{in,CO_2}}{\Delta q_{CO_2}}$$

- Using IZA database, the separation feasibility was tested for 346 zeolites, and 8 zeolites were found to be feasible.



가성빈

Seongbin Ga
School of Chemical Engineering
Pusan National University (PNU)
Republic of Korea

Email: sga00@pusan.ac.kr