Propane/Propylene Separation by PSA on SiCHA

Mona Khaligh, I.A. Karimi and S. Farooq
Department of Chemical and Biomolecular Engineering, National University of Singapore,
4 Engineering Drive 4,Singapore-117576
E-mail: mona@nus.edu.sg

Background

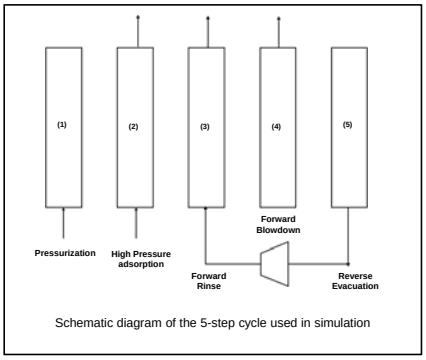
- Propane/propylene mixture comes from the thermal/catalytic cracking of hydrocarbons.
- The separated propylene has many uses, such as monomer feedstock for polypropylene elastomer production.
- Propylene must be at least 99.5 mol % pure.



- The propane fraction can be recycled to the cracking step or used separately as liquefied petroleum gas (LPG).
- Conventional cryogenic distillation method is not economic due to low relative volatility.
- Pressure Swing Adsorption (PSA) is an alternative that can save energy cost.
- Propylene is the extract product and the challenge is to achieve high purity and high recovery.



Proposed PSA Cycle



Schematic diagram of the 5-step cycle used in simulation

- Kinetic selectivity

$$\frac{K_{C_3H_6}}{K_{C_3H_8}}\sqrt{\frac{D_{C_3H_6}}{D_{C_3H_8}}}$$

- Equilibrium selectivity

$$\frac{K_{C_3H_6}}{K_{C_3H_8}}$$

- Orthogonal collocation method.
- 19 internal points.
- 50-70 cycle to reach steady state.

Governing Equations for PSA process

1. $$-D_l\frac{\partial^2 C_A}{\partial z^2}\pm\frac{\partial(vC_A)}{\partial z}+\frac{\partial C_A}{\partial t}+\frac{1-\varepsilon}{\varepsilon}\left(\frac{\partial \bar{q}_A}{\partial t}\right)=0$$

2. $$C\frac{\partial v}{\partial z}+\frac{\partial C}{\partial t}+\frac{1-\varepsilon}{\varepsilon}\left(\frac{\partial \bar{q}_A}{\partial t}+\frac{\partial \bar{q}_B}{\partial t}\right)=0$$

3. $$\frac{\partial \bar{q}_A}{\partial t}=k_A(q_A^*-\bar{q}_A)$$

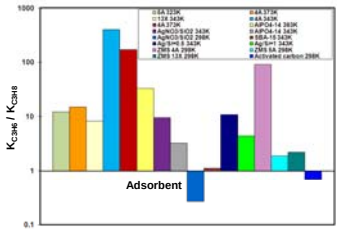
4. $$\frac{q_A^*}{q_{AS}}=\frac{b_A C_A}{1+b_A C_A+b_B C_B}$$

5. Appropriate boundary conditions applied for each step.

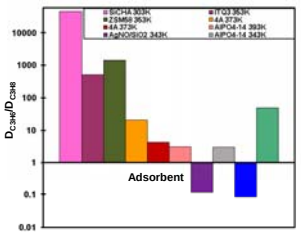
Model Asumptions

- The ideal gas law applies.
- The bed is isothermal.
- Langmuir isotherm.
- $K_{C_3H_8}=K_{C_3H_6}$
- Dispersed plug flow.
- LDF model with cycle time dependent Ω .

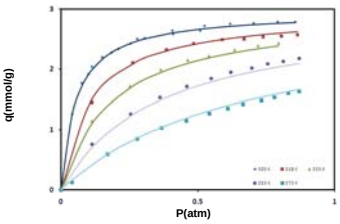
Literature Data



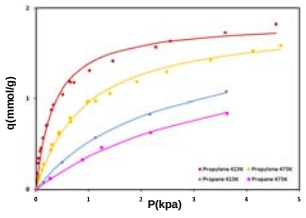
Equilibrium selectivity in various adsorbents



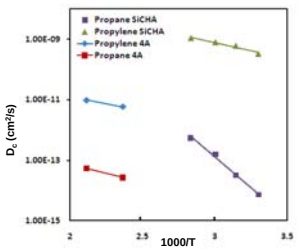
Diffusivity ratio in various adsorption



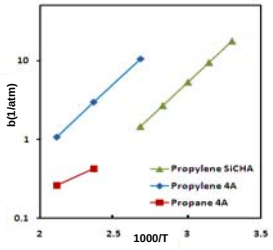
Adsorption isotherms for propylene in SiCHA including Langmuir fit.



Adsorption isotherms in 4A including Langmuir fit.

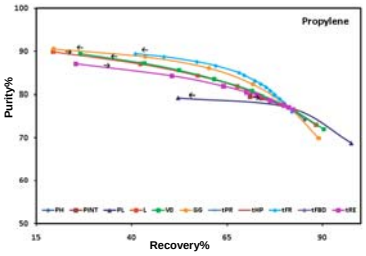


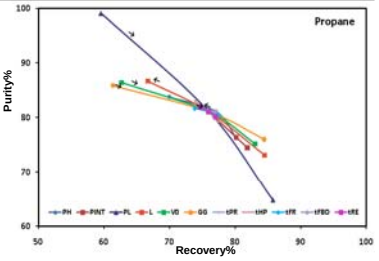
Arrhenius plot

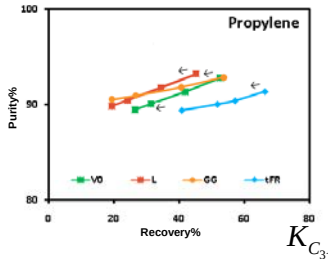


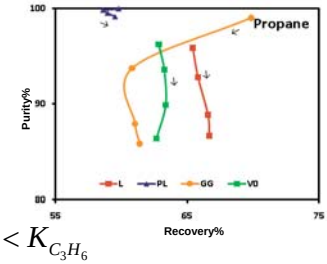
Temperature dependence of Langmuir constant

Results (each parameter increases in the direction of arrow)









$$K_{C_3H_8} < K_{C_3H_6}$$

Conclusions

- Among the commercial adsorbents evaluated so far in the literature for this separation, 4A zeolite and SiCHA are the most promising ones.
- We have achieved significant separation on SiCHA starting from a 50:50 mixture and further improvement seems possible.

Future works

- A pore diffusion model should be applied for more reliable assessment.
- Obtain equilibrium data for propane on SiCHA.

References

- D. H. Olson, M. A. Camblor, L. A. Villaescusa, G. H. Kuehl, Light hydrocarbon sorption properties of pure silica SiCHA and ITQ3 and high silica ZSM58, Microporous and Mesoporous Materials, 67, 2004, 27-33.
- D. M. Ruthven, S. C. Reyes, Adsorption separation of light olefins from paraffins, Microporous and Mesoporous Materials, 104, 2007, 59-66.
- C. A. Grande and A. E. Rodrigeus, Propane/Propylene sepration by pressure swing adsorption using zeolite 4A, Ind. Eng. Chem. Res. 44, 2005, 8815-8829.
- C. A. Grande and A. E. Rodrigeus, Propane/Propylene binary adsorption on zeolite 4A, Adsorption, 9, 2003, 321-329.
- J. Padin, S. U. Rege, R. T. Yang, *L. S. Cheng,* Molecular sieve sorbents for kinetic separation of propane/propylene, Chemical Engineering Science , 55, 2000, 4525-4535.
- S. U. Rege, J. Padin, R. T. Yang, Olefin/ Paraffin Separations by Adsorption: domplexation vs. Kinetic separation, AIChE, 44, 1998,799-809.
- F. A. Da Silva and A. E. Rodrigues, Propylene\Propane Separation by Vacuum Swing Adsorption Using 13X Zeolite,AIChE, 47, 2001, 341-357.
- N. Hedin, G. J. DeMartin, W. J. Roth, K. G. Strohmaier, S. C. Reyes, PFG NMR self-diffusion of small hydrocarbons in high silica DDR,CHA and LTA structures, Microporous and Mesoporous Materials, 109, 2008, 327–334.