

Adsorptive Ethylene Recovery from LDPE Off-Gas

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Abstract—The objective of this study was to verify experimentally the recovery of high-purity ethylene from LDPE off-gas by a vacuum swing adsorption process. Adsorbent for this purpose was prepared by the impregnation of AgNO₃ on Montmorillonite clay. The prepared adsorbent with an original substrate-shaped form shows high adsorption selectivities of light olefins to the corresponding paraffins. A 4-bed vacuum swing adsorption process using the above adsorbent, in which steps comprise adsorption (feeding), cocurrent rinse with ethylene product, countercurrent desorption (production) of ethylene by vacuum pump, pressurization-1 with paraffin stream, pressurization-2 with the rinse off-gas from the other bed and pressurization-3 with paraffin stream, was experimentally applied to recover ethylene from LDPE off-gas. Ethylene product purity of 99.95% could be obtained with the recovery of over 93%. The ethylene productivity of prepared adsorbent was 1.98 mol/kg·hr.

Key words: π -Complexation, Ethylene, Olefin Selective Adsorbent, LDPE Off-gas, Vacuum Swing Adsorption Process

INTRODUCTION

Ethylene is the most important building block in any petrochemical industry. The separation of ethylene from ethane and propylene from propane has been achieved conventionally by low temperature and/or high-pressure distillation. Demand for ethylene and propylene is ever increasing and mixtures including olefins produced in the petroleum refining process are often used as refinery fuel. Therefore, the recovery of olefins in this stream would be a substantial conservation of resources [Keller et al., 1992; Eldridge et al., 1993, 1998]. Among a number of alternative methods, separation based on π -complexation appears the most promising.

Separation via π -complexation is a sub-group of chemical complexation where the mixture is brought into contact with a second phase containing a complexing agent [Cotton and Wilkinson, 1966; King, 1987; Yang et al., 1995]. Transition metals, i.e., from Sc to Cu, Y to Ag and La to Au in the periodic table or their ions can form π -bonds with unsaturated hydrocarbons (olefins). These metals or their ions can form the normal σ bond to carbon and, in addition, the unique characteristics of the d orbitals in these metals or ions can form bonds with olefins in a nonclassical manner. This type of bonding is broadly referred to as π -complexation.

Electronic configurations of carbon and silver and metal-olefin coordination are shown in Table 1 and Fig. 1, respectively. Through chemical complexation it is possible to achieve high selectivity and capacity for the component to be bound due to stronger bonds than those formed by van der Waals force alone. However, π -bonds are still sufficiently weak to be broken by using simple engineering operations such as raising the temperature and decreasing the pres-

Table 1. Electronic configurations of carbon and silver element

Element	Shell									
	K		L		M		N			
C element (6)	1s	2s 2p	3s 3p 3d	4s 4p 4d 4f	5s 5p 5d 5f 5g					
	2	2 2								
Ag element (47)	1s	2s 2p	3s 3p 3d	4s 4p 4d 4f	5s 5p 5d 5f 5g					
	2	2 6	2 6 10	2 6 10	1					

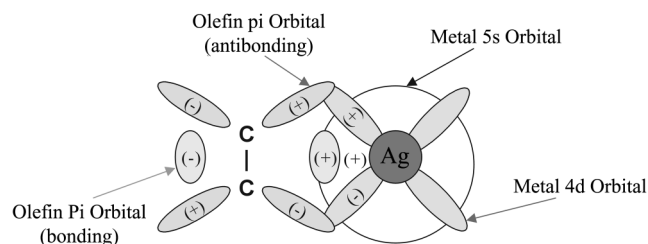


Fig. 1. Coordination between silver ion (Ag⁺) and ethylene.

sure. The early attempts for the separation of olefin/paraffin mixtures based on π -complexation employed liquid solutions containing silver (Ag⁺) or cuprous (Cu⁺) ions [Ho et al., 1988; Keller et al., 1992; Blytas, 1992; Eldridge, 1993]. There have been a number of studies with gas-solid systems based on π -complexation [Gilliland et al., 1941; Long, 1972; Hirai et al., 1985, 1992; Cen, 1991]. Gas-solid operations should be simpler as well as more efficient particularly by pressure swing adsorption process [Kim et al., 1995; Oh et al., 1998; Shin et al., 1998; Park et al., 2000; Na et al., 2001].

More recent efforts to find available sorbents and to prepare new sorbents for the separation of ethylene/ethane and propylene/propane by pressure swing adsorption, have appeared in the literature [Yang and Kikkiniades, 1995; Chen and Yang, 1995; Wu et al., 1997; Rege et al., 1998; Ramachandran et al., 1998; Cho et al., 1999, 2000,

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*This paper is dedicated to Dr. Youn Yong Lee on the occasion of his retirement from Korea Institute of Science and Technology.

2001; Han et al., 1999; Silva and Rodrigues, 2001; Choudary et al., 2002]. Especially, Yang et al. have prepared several kinds of new solid sorbents for selective light olefin adsorption over corresponding paraffin via π -complexation; Ag^+ -exchanged resins, monolayered CuCl/γ -alumina, monolayered CuCl /pillared clays and monolayered $\text{AgNO}_3/\text{SiO}_2$.

Until now, performance data by pressure swing adsorption process using silver impregnated adsorbent based on clay substrate have not been published in the literature.

This study is on the preparation of light olefin selective adsorbent in substrate-shaped form, and also the verification of light olefin purification from LDPE off-gas by vacuum swing adsorption process using this adsorbent.

EXPERIMENTAL

1. Adsorbent Preparation and Analyses

The substrate used in the present study is granular Montmorillonite clay of 1.0–2.0 mm. Typical Montmorillonite clay contains a relatively large amount of magnesium oxide among various clays. The pore size distribution of these substrates exists predominantly in the mesoporous region. The chemical used as a complexing agent was AgNO_3 (at least 99.8% purity) from Junsei Chemicals Co., Japan. For the preparation of olefin selective adsorbent, the incipient wetness technique was used. The impregnation method involves normally four steps: (a) pretreatment of the substrate with alkali solution and washing it with deionized water, (b) contacting and mixing the substrate with the impregnating solution for a certain period, (c) drying the resultant to remove the excess liquid, and (d) activating the material resulting from step (c) by thermal treatment at higher than 150 °C. The total quantity of the AgNO_3 solution is kept equal to the total known pore volume of the substrate. The imbibed solvent is removed by drying first with inert gas purge at room temperature followed by heating. The clay substrate was used in granular form (particle size of 8–12 mesh) and hence the eventual form of the prepared adsorbent by this impregnation method was kept in its original form of substrate. So further forming of prepared adsorbent for process application is not required. The physical properties of the substrate and the prepared adsorbent are shown in Table 2.

Nitrogen adsorption/desorption isotherms of clay substrate and prepared adsorbent were measured with ASAP analyzer (Micromeritics Co.) at 77 K. The results are shown in Fig. 2. Both clay substrate and prepared adsorbent give normal Type II adsorption isotherms, although their full adsorption/desorption isotherms exhibit Type H3 hysteresis by the IUPAC classification of hysteresis loops. Same results as our studies can be found in the literature [Rouquerol et al., 1999].

To investigate the nature of the active metal ion dispersed on the solid substrate, temperature programmed reduction (TPR) of several samples was measured by using a quartz micro-reactor fitted

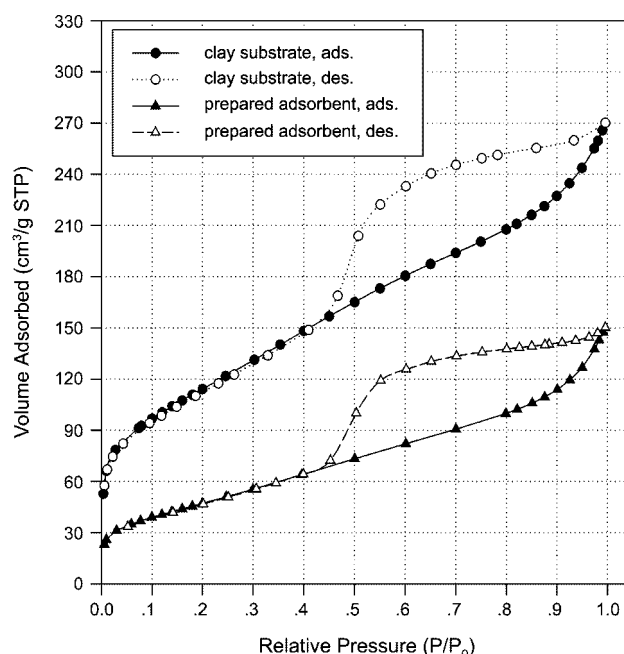


Fig. 2. Nitrogen isotherms of clay substrate and prepared adsorbent at 77 K.

Table 3. Chemical analyses of prepared adsorbent (0.4 g- AgNO_3 /g-substrate)

Component	Composition	Component	Composition
AgNO_3	27.6	CaO	0.6
SiO_2	49.8	MgO	2.0
Al_2O_3	11.7	Na_2O	1.6
Fe_2O_3	6.2	K_2O	0.5

with gas chromatograph with a thermal conductivity detector. TPR results showed the presence of one major peak with a shoulder and another small peak. These mean the presence of three types of silver species probably corresponding to AgNO_3 , Ag_2O and AgO .

Chemical composition of prepared adsorbent was analyzed with atomic absorption spectrometer and chemical wet analysis. The silver content of prepared adsorbent almost corresponded to the dosed amount in the preparation procedure when all of the silver species in prepared adsorbent are regarded as silver nitrate. Chemical composition of the adsorbent is summarized in Table 3.

2. Measurements of Adsorption/Desorption Equilibria

Adsorption and desorption equilibria were gravimetrically measured with two systems, i.e., Cahn 1100 microbalance and magnetic suspension balance (MSB). The prepared adsorbent was regenerated in the balance under the flow of ultra high purity helium gas at 210 °C, then adjusted to the measuring temperature and evacuated to 10^{-4} mmHg by using a turbo molecular pump. After each adsorption isotherm measurement, the desorption isotherm was also

Table 2. Physical properties of the substrate and the prepared adsorbent

Material	g- AgNO_3 /g-substrate [-]	Average pore size [Å]	BET surface area [m^2/g]	Pore volume [cm^3/g]
Substrate (clay)	Nil	40.3	392	0.42
Prepared adsorbent	0.4	34.0	172	0.23

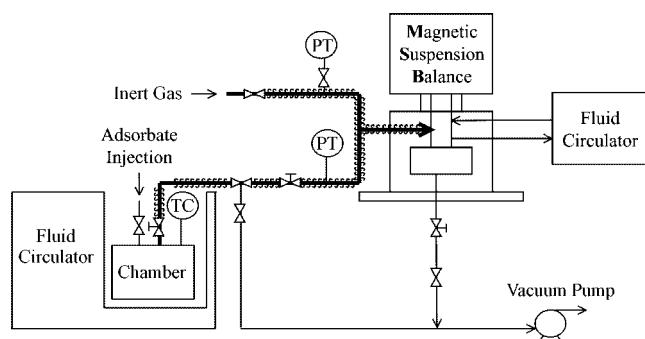


Fig. 3. Schematic diagram of magnetic suspension balance system.

measured to check the reversibility. Light olefins and paraffins used were the following: ethylene (Air Products & Chemicals Co., minimum purity 99.7%), ethane (Air Products & Chemicals Co., minimum purity 99.5%), propylene (Air Products & Chemicals Co., minimum purity 99.5%) and propane (Liquid Carbonic Co., minimum purity 99.5%). And the other gases which can exist in the feed, i.e. methane (minimum purity 99.99%), carbon monoxide (minimum purity 99.5%), carbon dioxide (minimum purity 99.99%), nitrogen (minimum purity 99.99%) and moisture were used. Isotherms of ethylene, ethane, propylene and propane were measured with Cahn 1100 microbalance and those of the other gases were measured with MSB system. The schematic MSB system is shown in Fig. 3.

3. Process Test

A pilot scale version of the pressure swing adsorption unit was designed and manufactured to operate automatically and connected to an LDPE off-gas stream at a petrochemical site. The schematic diagram of this unit is shown in Fig. 4. This ethylene purification system operated at ambient temperature is divided into two parts, i.e., the pretreatment part composed of two beds [250 mm (ID)×600 mm (H)×2 beds] in which activated carbon and silicagel adsorbents were multilayered with equal loading volume ratio in each

bed, and the main purification part [68 mm (ID)×2,000 mm (H)×4 beds] composed of four beds in which prepared $\text{AgNO}_3/\text{clay}$ adsorbent was loaded with the amount of 7.65 kg in each bed. The main function of pretreatment part is to remove C_3 , C_4 and heavier components. The regeneration of pretreatment bed was performed first by reducing the pressure from high feeding pressure of LDPE off-gas stream to almost ambient and then purging countercurrently with the effluent stream from a paraffin surge tank of the main purification part. One pretreatment bed for LDPE off-gas processing was operated at $4 \text{ kg/cm}^2\cdot\text{G}$ during 3 hours, while the other for adsorbent regeneration was operated at $0.1 \text{ kg/cm}^2\cdot\text{G}$ and ambient temperature and then vice versa. The operation pressures of feed buffer tank, olefin surge tank and paraffin surge tank were maintained at $4 \text{ kg/cm}^2\cdot\text{G}$, $0.2\text{--}0.4 \text{ kg/cm}^2\cdot\text{G}$ and $0.05\text{--}0.15 \text{ kg/cm}^2\cdot\text{G}$, respectively. In the purification part, the pressure in adsorption step was operated at 380–850 mmHg [ABS] and the lowest pressure during vacuum desorption was controlled at 25–40 mmHg [ABS].

RESULTS AND DISCUSSION

1. Equilibrium Isotherms

The adsorption/desorption characteristics were very much changed depending on impregnation amount of AgNO_3 and alkali treatments. Adsorption amounts of ethylene, ethane, propylene and propane on this prepared adsorbent were 1.15 mmol/g, 0.14 mmol/g, 1.30 mmol/g and 0.30 mmol/g at 1 atm and 25°C , respectively. The pure adsorption selectivity of olefin over the corresponding paraffin is very high. On the other hand, the pure adsorption amounts of impurities such as nitrogen, carbon monoxide, carbon dioxide and methane were less than 0.1 mmol/g at 50 mmHg and 25°C . The moisture on this adsorbent did not much affect the olefin adsorption characteristics.

The moisture also showed no chemical effects on this adsorbent and was easily removed by heating.

Isotherms of light olefins, light paraffins and several impurities are shown in Fig. 5 and Fig. 6.

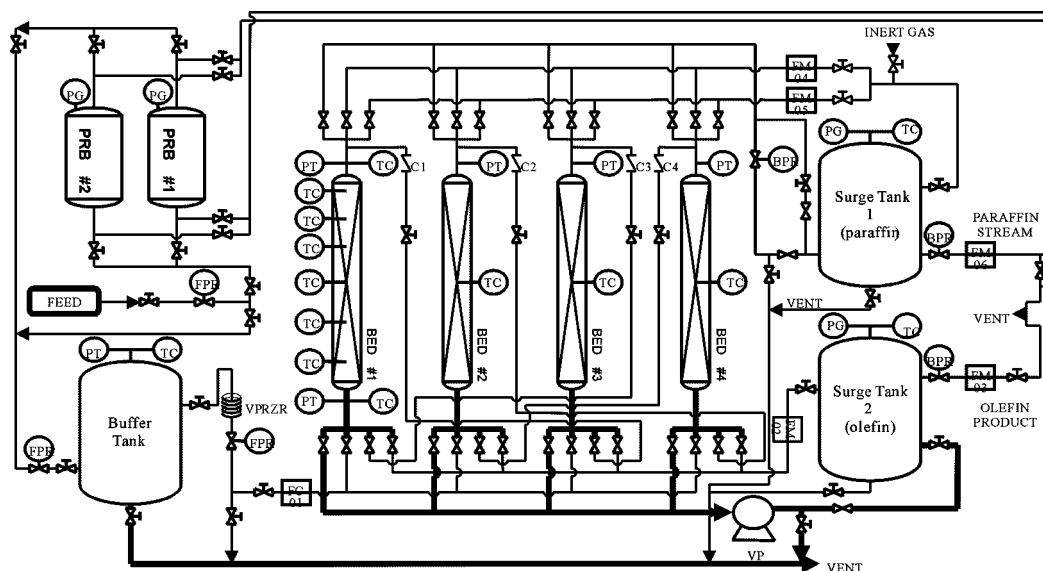


Fig. 4. Schematic diagram of adsorptive LDPE off-gas separation unit.

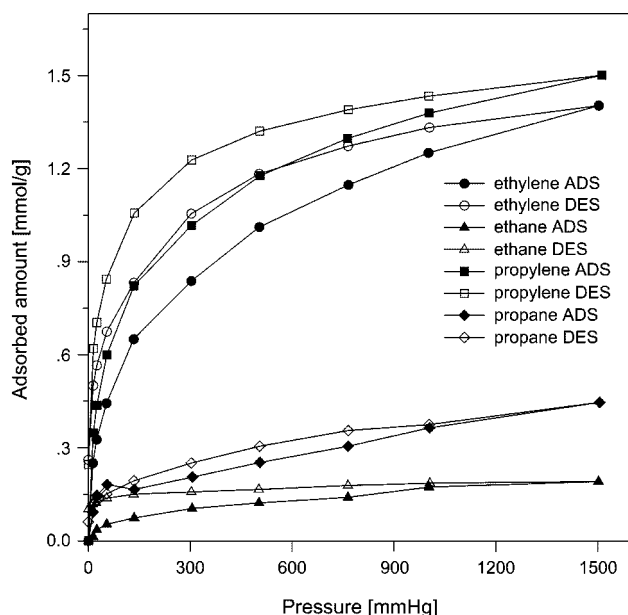


Fig. 5. Adsorption/desorption isotherms of light olefin and paraffin components at 25 °C.

2. Process Performance

In LDPE off-gas stream, ethylene (98.3%) is mainly contained and impurities such as nitrogen (840 ppm), carbon monoxide (20 ppm), carbon dioxide (0.22%), methane (40 ppm), ethane (0.92%), propane (60 ppm), propylene (trace), C_4 components (0.37%) and high carbon number solvent (870 ppm) are also contained.

Total hydrocarbon concentration except ethylene and ethane was reduced to less than 250 ppm by the pretreatment bed and then the pretreated stream was sent to the four bed vacuum swing adsorption process. This process is composed of six new steps as follows: feeding/adsorption (190 sec), cocurrent rinse with olefin product (170 sec), countercurrent desorption/production of olefin by vacuum pump (190 sec), pressurization-1 with paraffin stream (3 sec), pressurization-2 with the rinse off-gas from the other bed (170 sec) and pressurization-3 with paraffin stream (17 sec). The duration of one cycle was 760 sec. The effluent gas from a rinse step was sent to the other bed to recover an enriched ethylene portion. Step configurations with flow directions are shown in Fig. 7.

The definition of the performance criteria that characterize this

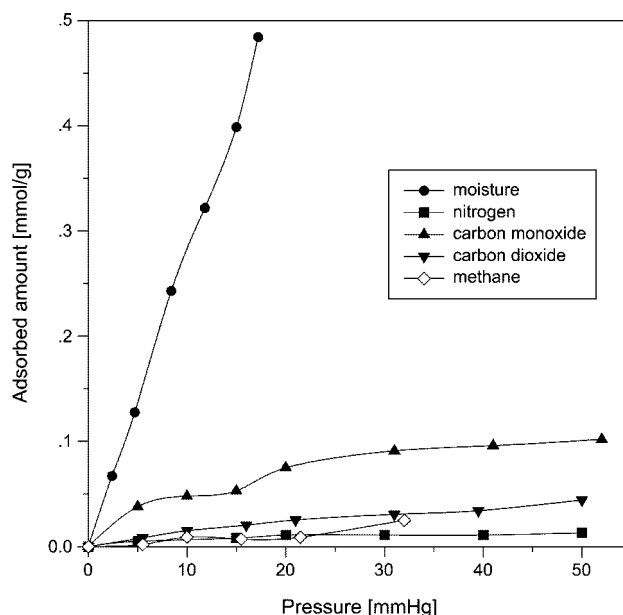


Fig. 6. Adsorption isotherms of moisture, nitrogen, carbon monoxide, carbon dioxide and methane at 25 °C.

VSA process provides a common basis:

$$\text{Purity (\%)} = \frac{\text{Amount of } C_2H_4 \text{ obtained in desorption step}}{\text{Amount of all gases obtained in desorption step}} \times 100$$

$$\text{Recovery (\%)} = \frac{(\text{Amount of } C_2H_4 \text{ obtained in desorption step} - \text{Amount of } C_2H_4 \text{ used in rinse step})}{\text{Amount of } C_2H_4 \text{ in adsorption step}} \times 100$$

$$\text{Productivity} = \frac{(\text{Amount of } C_2H_4 \text{ obtained in desorption step} - \text{Amount of } C_2H_4 \text{ used in rinse step})}{\text{Total sorbent amount} \times \text{total cycle time}}$$

When the purification process was operated with feed rate of 23.0SLPM and rinse flow rate of 4.65SLPM, ethylene product purity of 99.95% with the recovery of over 93% was obtained at steady state. At the same ethylene purity, the increase of feed flow rate results in the decrease of ethylene recovery and the decrease of feed flow rate results in the decrease of adsorbent productivity. Nitrogen, carbon monoxide, carbon dioxide, and methane components were passed through the bed with ethane component.

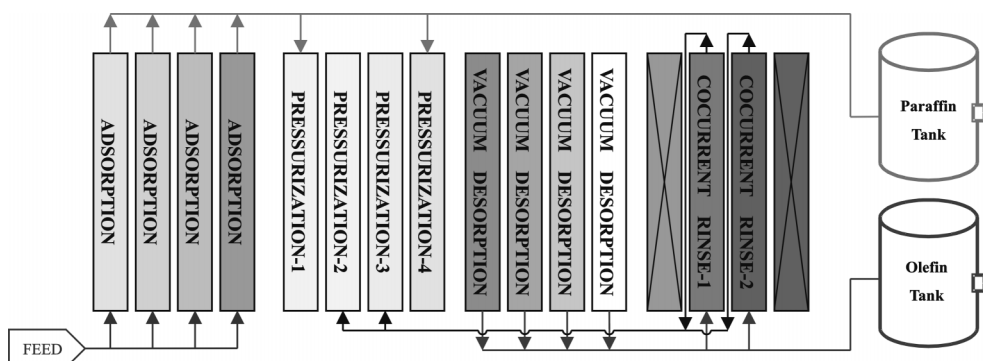


Fig. 7. Step configurations and flow directions of the pilot-scale unit.

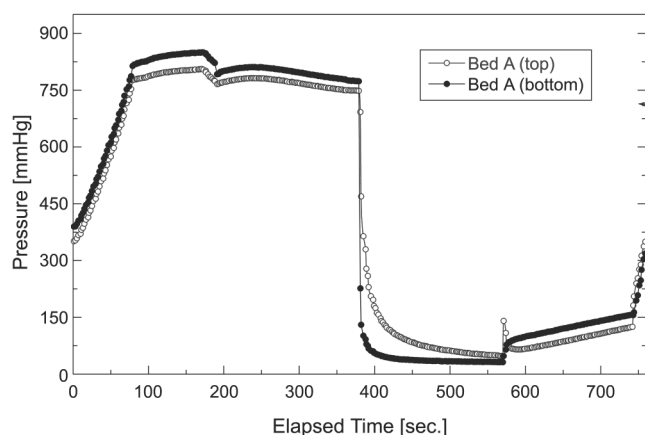


Fig. 8. Pressure histories during one cycle at dynamic steady state.

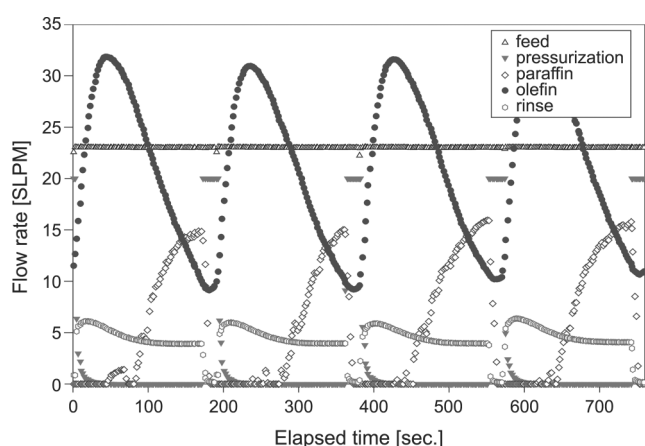


Fig. 9. Flow histories during one cycle at dynamic steady state.

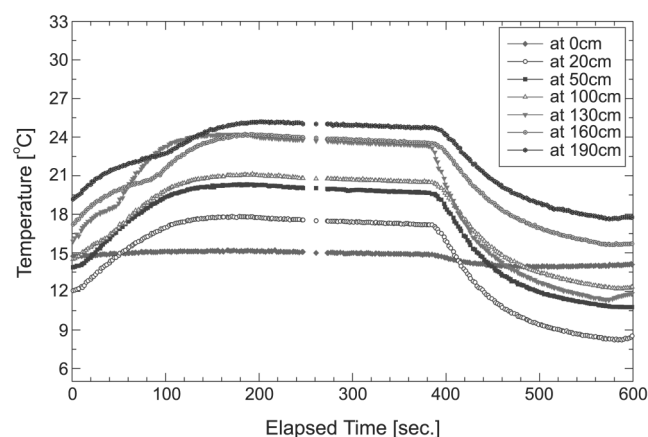


Fig. 10. Temperature histories during one cycle at dynamic steady state.

First, LDPE off-gas stream was suitably pretreated with commercial adsorbents to remove propylene and heavier components to less than 250 ppm, and then the vacuum swing process with $\text{AgNO}_3/\text{clay}$ adsorbent could be suitably applied to obtain a high purity ethylene of over 99.95%. The ethylene productivity of loaded adsorbent was 1.98 mol/kg·hr.

Experimental pressure, flow and temperature excursions during

one cycle at dynamic steady state are shown in Fig. 8, Fig. 9 and Fig. 10, respectively. In Fig. 10, some data are intentionally cut for a clear appearance of each symbol.

CONCLUSIONS

Adsorbent for light olefin/paraffin separations via π -complexation was prepared by the impregnation of AgNO_3 on mesoporous Montmorillonite clay substrate. This olefin selective adsorbent with an original substrate-shaped form shows high olefin selectivity. In this study, the pure adsorption selectivity of ethylene over ethane is 8.2 at 760 mmHg and 25 °C.

The 4-bed vacuum swing adsorption process combined with an appropriate pretreatment of 2-bed experimentally demonstrates that high-purity ethylene from LDPE off-gas can be obtained with high recovery. This adsorption process can also be applied to many ethylene streams in a (petro)-chemical complex for ethylene enrichment, purification and removal.

REFERENCES

- Blytas, G. C., "Separation of Unsaturates by Complexing with Non-Aqueous Solutions of Cuprous Salts," Separation and Purification Technology, Chap. 2, Li, N. N. and Calo, J. M. eds., Dekker, New York (1992).
- Cen, P. L., "Simultaneous Physical and Chemical Adsorption of Ethylene and Cu(I) NaY Zeolite," Fundamentals of Adsorption, Mersmann, A. B. and Scholl, S. E. eds., Engineering Foundation, New York, 191 (1991).
- Chen, J. P. and Yang, R. T., "Molecular Orbital Study of Selective Adsorption of Simple Hydrocarbons on Ag^+ and Cu^+ Exchanged Resins and Halides," *Langmuir*, **11**, 3450 (1995).
- Cheng, L. S. and Yang, R. T., "Monolayer Cuprous Chloride Dispersed on Pillared Clays for Olefin-Paraffin Separations by π -Complexation," *Adsorption*, **1**, 61 (1995).
- Cho, S. H., Han, S. S., Kim, J. N., Choudary, N. V., Kumar, P. and Bhat, S. G. T., "Light Olefin/Paraffin Separation by Vacuum Swing Adsorption Process," 1999 AIChE Annual Meeting, Dallas, TX, Oct. 31-Nov. 5, T1027-PSA/TSA I (1999).
- Cho, S. H., Han, S. S., Kim, J. N., Choudary, N. V., Kumar, P. and Bhat, S. G. T., "Adsorbents and Methods for the Separation of Ethylene and Propylene and/or Unsaturated Hydrocarbons from Mixed Gases," Korean Patent, 0279881 (2000).
- Cho, S. H., Han, S. S., Kim, J. N., Choudary, N. V., Kumar, P. and Bhat, S. G. T., "Adsorbents, Methods for the Preparation and Method for the Separation of Unsaturated Hydrocarbons for Gas Mixtures," US Patent, 6315816 B1 (2001).
- Choudary, N. V., Kumar, P., Bhat, S. G. T., Cho, S. H., Han, S. S. and Kim, J. N., "Adsorption of Light Hydrocarbon Gases on Olefin Selective Adsorbent," *Ind. Eng. Chem. Res.*, **41**, 2728 (2002).
- Cotton, F. A. and Wilkinson, G., "Advanced Inorganic Chemistry," 2nd ed., Chaps. 25 and 28, Interscience, New York (1966).
- Da Silva, F. A. and Rodrigues, A. E., "Propylene/Propane Separation by Vacuum Swing Adsorption Using 13X Zeolite," *AIChE J.*, **47**(2), 341 (2001).
- Eldridge, R. B., "Olefin/Paraffin Separation Technology: A Review," *Ind. Eng. Chem. Res.*, **32**, 2208 (1993).

- Gilliland, E. R., Bliss, H. L. and Kip, C. E., "Reactions of Olefins with Solid Cuprous Halide," *J. Amer. Chem. Soc.*, **63**, 2088 (1941).
- Han, S. S., Kim, J. N. and Cho, S. H., Choudary, N. V., Kumar, P. and Bhat, S. G. T., "Adsorbents for Light Alkane/Alkene Separation," The 8th APCChE Congress, Aug. 16-19, Seoul, Korea, 1777 (1999).
- Hirai, H., "Polymer Complex for the Separation of Carbon Monoxide and Ethylene," *Polymers for Gas Separation*, Chap. 7, Toshima, N. ed., VCH Publishers, New York, 221 (1992).
- Hirai, H., Hara, S. and Komiyama, M., "Polystyrene-Supported Aluminum Silver Chloride as a Selective Ethylene Adsorbent," *Angew. Makromol. Chem.*, **130**, 207 (1985).
- Ho, W. S., Doyle, G., Savage, D. W. and Pruett, R. L., "Olefin Separations via Complexation with Cuprous Diketonate," *Ind. Eng. Chem. Res.*, **27**, 334 (1988).
- Keller, G. E., Marcinkowsky, A. E., Verma, S. K. and Williamson, K. D., "Olefin Recovery and Purification via Silver Complexation," *Separation and Purification Technology*, Chap. 3, Li, N. N. and Calo, J. M. eds., Dekker, New York (1992).
- Kim, W. G., Yang, J. Y., Han, S. S., Cho, C. H., Lee, C. H. and Lee, H. J., "Experimental and Theoretical Study on H₂/CO₂ Separation by a Five-Step One-Column PSA Process," *Korean J. Chem. Eng.*, **12**, 503 (1995).
- King, C. J., "Separation Process Based on Reversible Chemical Complexation," *Handbook of Separation Process Technology*, Rousseau, R. W. ed., Chap. 15, Wiley, New York (1987).
- Long, R. B., "Separation of Unsaturates by Complexing with Solid Copper Salts," *Recent Developments in Separation Science*, Vol. 1, Li, N. N. ed., CRC Press, Cleveland, OH (1972).
- Na, B. K., Koo, K. K., Eum, H. M., Lee, H. U. and Song, H. K., "CO₂ Recovery from Flue Gas by PSA Process using Activated Carbon," *Korean J. Chem. Eng.*, **18**, 220 (2001).
- Oh, M. and Moon, J. K., "Optimisation of Cycle Time and Feed Pressure on Rapid Pressure Swing Adsorption in Separation of N₂/O₂," *HWAHAK KONGHAK*, **36**, 196 (1998).
- Park, J. H., Kim, J. N. and Cho, S. H., "Performance Analysis of Four-Bed H₂ PSA Process Using Layered Bed," *AIChE J.*, **46**(4), 790 (2000).
- Ramachandran, R., Dao, L. H. and Brook, B., "Method Producing Unsaturated Hydrocarbons and Separating the Same from Saturated Hydrocarbons," US patent, 5365011 (1998).
- Rege, S. U., Padin, J. and Yang, R. T., "Olefin/Paraffin Separations by Adsorption: π -Complexation vs. Kinetic Separation," *AIChE J.*, **44**(4), 799 (1998).
- Rouquerol, F., Rouquerol, J. and Sing, K., "Adsorption by Powders and Porous Solids: Principles, Methodology and Applications," Academic Press, London (1999).
- Safarik, D. J. and Eldridge, R. B., "Olefin/Paraffin Separations by Reactive Absorption: A Review," *Ind. Eng. Chem. Res.*, **37**, 2571 (1998).
- Shin, H. S. and Suh, S. S., "Performance Analysis of a Multi-Bed PSA Process to Simulate a Countercurrent Flow of Adsorbent," *HWAHAK KONGHAK*, **36**, 930 (1998).
- Wu, Z., Han, S. S., Cho, S. H., Kim, J. N., Chue, K. T. and Yang, R. T., "Modification of Resin-Type Adsorbents for Ethane-Ethylene Separation," *Ind. Eng. Chem. Res.*, **36**, 2749 (1997).
- Yang, R. T. and Kikkinides, E. S., "New Sorbents for Olefin/Paraffin Separations by Adsorption via π -Complexation," *AIChE J.*, **41**(3), 509 (1995).