Adsorption 11: 621–624, 2005

Propylene Recovery from Propylene/Propane/Nitrogen Mixture by PSA Process

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Abstract. This study is on the process performance (purity, recovery and productivity) of a four-bed bench-scale PSA unit [1000 mm (L) × 25 mm (ID) × 4 beds], with which is applied to enrich propylene from propylene/propane/nitrogen gas mixture (35 mol% propylene, 15 mol% propane, 50 mol% nitrogen). Adsorbent, i.e. $AgNO_3$ impregnated on silica substrate, was prepared and loaded in the above PSA unit. The unit was operated at the pressure of 25–870 mmHg and at the temperature of 10–70°C. By a four-bed PSA process at 50°C, the propylene product purity and recovery were 91.9 mol% (7.0 mol% propane, 1.1 mol% nitrogen) and 86.5%, respectively. More than 99% of nitrogen was removed from the feed. The propylene productivity by the process was 0.89 mol/(kg·hr).

Keywords: adsorption, propylene, polypropylene process off-gas, π-complexation, pressure swing adsorption

1. Introduction

Propylene is the most important building block in any petrochemical industry. The separation of propylene from propane has been achieved conventionally by low temperature and/or high-pressure distillation. This makes the propylene/propane mixture one of the most energy-expensive separations because of the low relative volatility. Demand for propylene is ever increasing. Propylene mixtures produced in the petroleum refining process and unreacted propylene are often used as refinery fuel. Therefore, the recovery of olefins in this stream would be a substantial conservation of resources (Eldridge, 1993; Keller et al., 1992; Safarik et al., 1998). One example of light olefin recovery units is an additional application to conventional polypropylene manufacturing process. This application can result in the reuse of substantial raw material, the reduction of polypropylene manufacturing cost and more ecofriendly polypropylene manufacturing system. Many researchers (Padin et al., 2000; Grande et al., 2001, 2002; Da Silva et al., 2001; Rege et al., 2002; Han et al., 2002) have studied theoretically and practically on adsorptive propane/propylene separations using commercial and newly prepared sorbents. Yang (Padin et al., 2000; Rege et al., 2002) has recently studied on new sorbents for propane/propylene separation by π-complexation. BOC Gases Co. has already performed semi-commercial gaseous adsorption process test to recover propylene from polypropylene process off-gas stream.

This study is on the process performance (purity, recovery and productivity) of a bench-scale vacuum swing adsorption unit, with which is applied to recover propylene from simulated polypropylene process off-gas. Newly prepared adsorbent is used in the bench-scale unit.

2. Adsorbent Preparation and Adsorption Characteristics

The substrate used to prepare an adsorbent in the present study is the spherical silica of 0.5–2.5 mm.

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The pore size distribution of the substrate exists predominantly in 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 propylene selective adsorbent, impregnation method, in detail, incipient wetness technique was used. The impregnation method involves normally four steps; (a) thermal pretreatment of the substrate in dry gas environment, (b) contacting and mixing the substrate with the impregnating $AgNO_3$ solution, (c) drying the resultant to remove the solvent and (d) activation of the material resulted from step (c) by thermal treatment. The silica substrate for this preparation is originally made of spherical shape and hence the eventual shape of the prepared adsorbent by this impregnation method is kept in its original form of the substrate. The mechanical strength of prepared adsorbent is comparable to commercial activated alumina. Physical properties of a substrate and a prepared adsorbent are shown in Table 1. The silver content in prepared adsorbent almost corresponded to dosed amount in the above preparation procedure as all of silver species are regarded as silver nitrate. The full nitrogen adsorption/desorption isotherms on both silica substrate and prepared adsorbent at 77 K exhibit Type H2 hysteresis by the IUPAC classification of hysteresis loops. Same results as our studies can be found in the literature (Rouquerol et al., 1999). The prepared adsorbent contains silicon compound with more than 60 wt%.

Adsorption isotherms were gravimetrically measured with two systems, i.e., Cahn 1100 microbalance and magnetic suspension balance (MSB). The adsorption/desorption characteristics were so much changed depending on impregnation amount of $AgNO_3$. Adsorption isotherms of propylene and propane depending on temperature on the above prepared adsorbent are shown in Fig. 2. Adsorbed amounts of propylene and propane on the prepared adsorbent were 1.80 mmol/g and 0.75 mmol/g at 1atm and 25°C, respectively. Adsorbed amounts of both propylene and propane were decreased as adsorption temperature was increased, but the propylene selectivity over propane was increased. The adsorption rates of both propane and propylene were reasonably fast.

On the other hand, the pure adsorption amounts of impurities such as nitrogen, oxygen, carbon monoxide, carbon dioxide and methane were less than 0.15 mmol/g at 0.2 kg_f/cm^2 and 25°C. The impurities adsorbed on the adsorbent are easily desorbed when the adsorbent is heated. Adsorption isotherms of impurities are shown in Fig. 3.

Table 1. Physical properties of the substrate and the prepared adsorbent.

Material	BET surface area (m^2/g)	Pore volume (m^3/g)	Average pore diameter (Å)	Particle size (mm)
Silica (substrate)	719	0.52	28.9	0.5–2.5
Prepared adsorbent	268	0.22	32.9	0.5–2.5

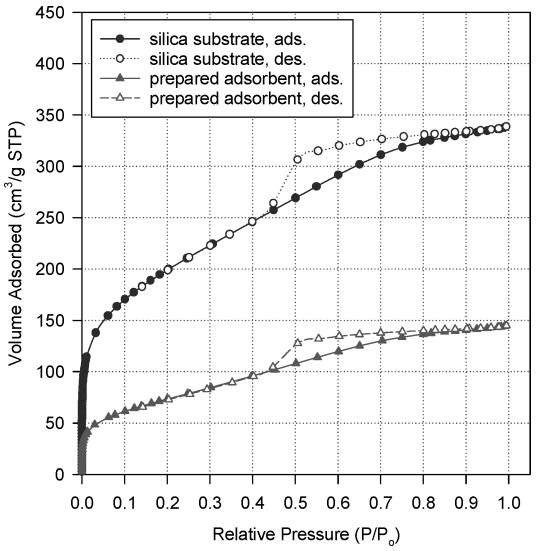

Figure 1. Nitrogen adsorption/desorption isotherms at 77 K.

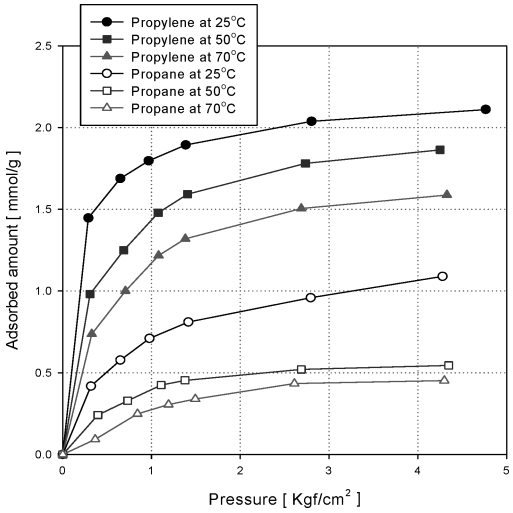

Figure 2. Adsorption isotherms of propylene and propane.

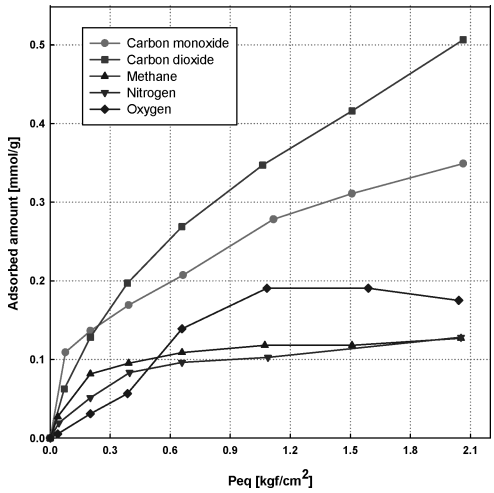

Figure 3. Adsorption isotherms of impurities at 25°C.

3. Process Description and Experimental Results

3.1. Pressure Swing Adsorption Unit and Process Description

A bench-scale pressure swing adsorption unit was designed and constructed to operate automatically. The schematic is shown in Fig. 4. The unit operated at less than 55°C was comprised of four adsorption beds [25 mm (ID) × 1000 mm (H) × 4 beds], in which prepared $AgNO_3$/silica adsorbent was loaded. An electric heating jacket was installed to adjust adsorption column temperature to the outer wall of each bed. The jacket was uncovered as the unit was operated at ambient temperature. The operation pressure of olefin surge tank and paraffin surge tank was maintained at 920 mmHg and at 870 mmHg, respectively. The pressure in adsorption step was maintained at 800–865 mmHg and the lowest pressure in vacuum desorption step was adjusted to 25–35 mmHg. A polypropylene process off-gas stream, for an example, contains 49.71% nitrogen, 2.58% ethylene, 0.28% ethane, 29.86% propylene, 13.59% propane, 0.02% C_4's, and 3.74% C_5 & C_6. Referring to the above off-gas composition, a gas mixture in which is composed of 50% nitrogen, 35% propylene and 15% propane, was prepared and used as a feed to the bench-scale unit.

The separation process is comprised of five steps as follows; pressurization-1 with paraffin stream (12 seconds), adsorption/feeding (168 seconds), recovery of propylene from the rinse off-gas stream from the other bed (180 seconds), cocurrent rinse with propylene product (180 seconds), and countercurrent desorption/production of propylene (108 seconds). The duration of one cycle is 720 seconds.

3.2. Process Performance

When a five-step and four-bed process already explained in Section 3.1 was applied with feed rate of 2500 SCCM and rinse flow rate of 1380 SCCM at ambient temperature (16.8°C), the propylene product purity was 90.08% with the recovery of 77.8%. The product contains nitrogen 0.44% and propane 9.48%. The removal rates of nitrogen and propane were 99.7% and 80.9%, respectively. The propylene productivity was 0.82 mol/(kg·hr). When the rinse flow rate was increased to 1580 SCCM with the same feed flow rate, propylene product purity was increased to 93.09%

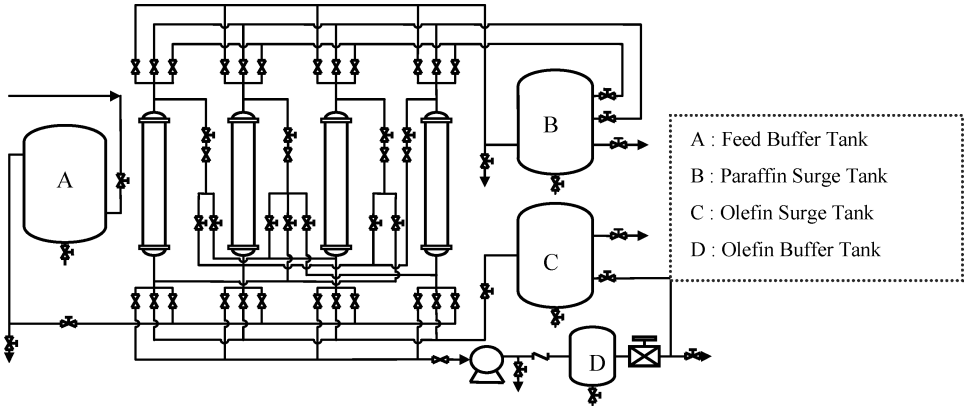

Figure 4. Schematic diagram of adsorptive separation unit.

containing 0.48% nitrogen and 6.43% propane with the recovery of 72.0%. Nitrogen removal rate was same with the above, but propane 88.4% of propane was removed. The propylene productivity was a little decreased to 0.75 mol/(kg·hr).

An electric heating mantle system was applied to the outer surface of each adsorption bed to enhance adsorption and desorption rates. When the separation process was operated at the feed rate of 2500 SCCM and the rinse flow rate of 1214 SCCM with setting to 50°C at the outer surface of each bed, the propylene product purity was 91.9% with the recovery of 86.4%. The product contains 1.15% nitrogen and 6.98% propane. The removal rates of nitrogen and propane were 99.3% and 84.7%, respectively. The propylene productivity was 0.89 mol/(kg·hr). As the rinse flow rate was increased to 1750 SCCM with the same feed flow rate, propylene product purity was increased to 97.20% with the recovery of 79.4%. The product contains 0.38% nitrogen and 2.42% propane. Nitrogen and propane removal rates were 99.8% and 95.4%, respectively. The propylene productivity at that time was 0.83 mol/(kg·hr). As the unit was operated at higher adsorption/desorption temperature (about at 50°C), not only propylene product purity and recovery, but the propylene productivity was also increased. To get higher propylene purity, it was demanded to sacrifice the propylene recovery.

The existence of nitrogen results in thermal resistance during desorption step and diffusional resistance during adsorption step to both propylene and propane in the mixture.

4. Conclusion

The separation of propylene from propane is an important and difficult. It is more difficult to obtain high purity propylene from propylene/propane mixture with additional impurities (ex. nitrogen).

Newly prepared adsorbent for the separation of propylene from a mixture containing propylene, propane and nitrogen is introduced. This adsorbent is propylene-selective by π-complexation and has enough mechanical strength. A five-step and four-bed pressure swing adsorption unit loaded with the prepared adsorbent was applied to separate propylene from a simulated gas (50% nitrogen, 35% propylene, and 15% propane). The propylene purity of 97.20% could be obtained with the recovery of 79.4%. Consequently, the five-step PSA process with this type of adsorbent shows the applicability to the recovery of propylene from polypropylene process off-gas.

Acknowledgments

This research was supported by Carbon Dioxide Reduction & Sequestration R&D Center under 21st Century Frontier R&D Program.

References

Da Silva, F.A. and A.E. Rodrigues, "Propylene/Propane Separation by Vacuum Swing Adsorption Using 13X Zeolite," *AIChE J.*, **47**, 341–357 (2001).

Eldridge, R.B., "Olefin/Paraffin Separation Technology," *Ind. Eng. Chem. Res.*, **32**, 2208–2212 (1993).

Grande, C.A., C. Gigola, and A.E. Rodrigues, "Adsorption of Propane and Propylene in Pellets and Crystals of 5A Zeolite," *Ind. Eng. Chem. Res.*, **41**, 85–92 (2002).

Grande, C.A. and A.E. Rodrigues, "Adsorption Equilibria and Kinetics of Propane and Propylene in Silica Gel," *Ind. Eng.Chem. Res.*, **40**, 1686–1693 (2001).

Han, S.S., J.H. Park, J.N. Kim, and S.H. Cho, "Study on Propylene/Propane Separation by Gaseous Adsorption Technology," in *Proceedings of the 6th International Symposium on Separation Technology between Korea and Japan*, 2002, pp. 501–504.

Keller, G.E., A.E. Marcinkowsky, S.K. Verma, and K.D. Williamson, "Olefin Recovery and Purification via Silver Complexation," in *Separation and Purification Technology*, N.N. Li and J.M. Calo (Eds.), pp. 59–83, Dekker, New York, 1992.

Padin, J., S.U. Rege, R.T. Yang, and L.S. Cheng, "Molecular Sieve Sorbents for Kinetic Separation of Propane/Propylene," *Chem. Eng. Sci.*, **55**, 4525–4535 (2000).

Rege, S.U. and R.T. Yang, "Propane/Propylene Separation by Pressure Swing Adsorption: Sorbent Comparison and Multiplicity of Cyclic Steady State," *Chem. Eng. Sci.*, **57**, 1139–1149 (2002).

Rouquerol, F., J. Rouquerol, and K. Sing, *Adsorption by Powders and Porous Solids: Principles, Methodology and Applications*, pp. 288–399, Academic Press, London, 1999.

Safarik, D. J. and R.B. Eldridge, "Olefin/Paraffin Separations by Reactive Absorption," *Ind. Eng. Chem. Res.*, **37**, 2571–2581 (1998).