Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Vacuum Pressure Swing Adsorption to Produce Polymer-Grade Propylene

Carlos A. Grande[a]; Frank Poplow[b]; Alírio E. Rodrigues[a]
[a] LSRE - Laboratory of Separation and Reaction Engineering, Associate Laboratory LSRE/LCM, Department of Chemical Engineering, Faculty of Engineering, University of Porto, Porto, Portugal [b] BASF SE, Ludwigshafen, Germany

Online publication date: 02 June 2010

To cite this Article Grande, Carlos A. , Poplow, Frank and Rodrigues, Alírio E.(2010) 'Vacuum Pressure Swing Adsorption to Produce Polymer-Grade Propylene', Separation Science and Technology, 45: 9, 1252 — 1259
To link to this Article: DOI: 10.1080/01496391003652767
URL: http://dx.doi.org/10.1080/01496391003652767

Separation Science and Technology, 45: 1252–1259, 2010

ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496391003652767

Taylor & Francis
Taylor & Francis Group

Vacuum Pressure Swing Adsorption to Produce Polymer-Grade Propylene

Carlos A. Grande,[1] Frank Poplow,[2] and Alírio E. Rodrigues[1]
[1]*LSRE – Laboratory of Separation and Reaction Engineering, Associate Laboratory LSRE/LCM, Department of Chemical Engineering, Faculty of Engineering, University of Porto, Porto, Portugal*
[2]*BASF SE, Ludwigshafen, Germany*

We have evaluated the Vacuum Pressure Swing Adsorption (VPSA) technology to separate propane–propylene streams to produce polymer-grade propylene. Zeolite 4A is used as kinetic adsorbent since propylene diffuses much faster than propane. A single VPSA process is able to produce propylene with purity higher than 99.6%. However, propylene recovery is only 67% and therefore a second stage is used. In this VPSA unit, zeolite 4A with smaller crystal radius is employed to reduce kinetic limitations. The second VPSA (tail unit) produces purified propane and recovers propylene that is recycled to the feed of the first VPSA (front unit). Linking these two VPSA units allows us to produce polymer-grade propylene (PGP) recovering 95.9% of the propylene. Comparing the performance of this process with distillation, there is a significant decrease in the separation volume. However, further efforts are necessary to reduce the power consumption of VPSA which is still slightly higher than for distillation.

Keywords distillation; kinetic adsorbents; Pressure Swing Adsorption; propylene; zeolite 4A

INTRODUCTION

Olefins are fundamental building blocks for the production of commodities. Unfortunately, the energy consumed in their purification is high (1,2). Ethylene and propylene are often obtained in mixtures with their paraffin homologues (ethane and propane, respectively). Olefin-paraffin separations are among the most energy-intensive processes in chemical industry (1); they are commonly performed in distillation towers (C_2 and C_3 splitters) with over 100 theoretical plates. High reflux ratios are necessary and vapor compression may be used for heat integration. High oil prices have boosted research of more efficient processes. Several reports indicate some of the alternative technologies that can be employed (2–4). Intensive research is being performed in membranes (5) and adsorption (6–12) processes to be considered as alternative technologies to distillation.

Vacuum Pressure Swing Adsorption (VPSA) has been under research for more than one decade using commercial (6–16) and tailor-made adsorbents (17–22). It was already shown that using zeolite 4A propylene streams with high purity can be obtained (10,14). Among many of the commercial adsorbents tested, zeolite 4A presented excellent properties to be employed in the VPSA process; the diffusion of propane within micropores is extremely slow (23) significantly reducing the amount of propane adsorbed and desorbed per cycle. It was previously shown that micropore diffusion strongly limits the adsorption rate of propane (23–25) and thus we can control its adsorption or desorption by controlling the size of zeolite crystals (25).

The main drawback of previously investigated VPSA processes is a relatively low propylene recovery of 84% for a purity of 99.4%, lower than PGP (polymer-grade propylene) specifications (10). Increasing purity to values higher than 99.5%, resulted in a further decrease of recovery. Furthermore, the low evacuation pressure of 10 kPa resulted in high power consumption (10). It should also be pointed out that these results were obtained in laboratory experiments with the column operating under non-adiabatic conditions exchanging significant amounts of heat with the surroundings.

In this work we present a complete strategy to separate propane and propylene streams by VPSA technology achieving PGP and high propylene recovery. A process comprising two different VPSA units operating in series was designed. Details of different cyclic schemes and the effect of different operating conditions are studied. Commercial adsorbent zeolite 4A with different crystal sizes was used for simulations of both VPSA units. The results in this work correspond to process simulation supported by strong experience using this adsorbent in laboratory VPSA units (6,10,15,23,25,26). Furthermore, the energy consumption and separation volume required by this new dual-VPSA strategy was compared with the requirements for distillation.

Received 23 November 2009; accepted 26 January 2010.
Address correspondence to Professor Alírio E. Rodrigues, Department of Chemical Engineering, Rua Dr. Roberto Frias, University of Porto, Porto 4200-465, Portugal. Tel.: +351225081671; Fax: +351225081674. E-mail: arodrig@fe.up.pt

PROCESS DESIGN AND OPERATING CONDITIONS

The specifications of the stream to be separated as well as the operating conditions of the final products (separation task) are detailed in Table 1.

The design of the VPSA process was performed using a detailed mathematical model developed previously in our laboratory (6,15,16). This model assumes that the adsorbent is bi-disperse, although for this specific case the micropore diffusion controls the diffusion rate within the particles. The model also includes three different energy balances (adsorbent, gas, and column wall) and the Ergun equation to take into account the pressure drop within the column. The adsorption equilibrium of propane and propylene was described with the multisite Langmuir model. This equilibrium model was validated against experimental data in single component and binary mixtures in manometric apparatus and fixed-beds (10,25,26). The Darken equation was employed to describe the crystal diffusivity variations with adsorbed phase concentration (25). Adsorption equilibrium and kinetic parameters of propane and propylene in zeolite 4A are detailed in Table 1. The system of PDEs (partial differential equations) was solved with the central finite difference method with 400 nodes in the spatial domain.

Using zeolite 4A as adsorbent, the temperature of the VPSA process should be within 423–463 K (14). We have also previously observed that the unit productivity of the VPSA unit can be increased if the total pressure of the system increases to 5 bar (10). These two operating conditions (pressure and temperature) of the VPSA unit are not coincident with the feed conditions as shown in Table 1. For this reason, the stream should be heated to 423 K and compressed to 5 bar before entering to the process.

The separation process proposed in this work is a dual-VPSA process where two VPSA units operate in series. The first unit, named front VPSA unit, intends to obtain propylene with a minimum purity of 99.5%, complying propylene polymer grade (PGP) specification. The recovery of the front VPSA is not high and thus the propane-rich stream still has much propylene that can be recovered in a second VPSA unit, the tail VPSA. The operational objectives of the two VPSA units are radically different: in the front unit, the objective is to purify the most adsorbed compound (propylene) while in the tail unit the main objective is to purify the less adsorbed compound (propane). Details about the operation of each of these individual units are discussed in the next two sections, followed by a discussion of the process integration where power consumption and total separation volumes are accounted for.

TABLE 1
Feed inlet conditions and product specifications to be satisfied by the separation process. A binary mixture of propane and propylene is considered

	Feed	C_3H_6-rich stream	C_3H_8-rich stream
Flowrate	31.25 ton/h		
Molar fraction C_3H_6	0.40	>0.995	<0.035
Pressure (abs)	2.5 bar	25 bar	4.5 bar
Temperature	323 K	323 K (liquid)	Not specified

FRONT VPSA: PRODUCTION OF POLYMER-GRADE PROPYLENE

The design of a VPSA unit to produce polymer-grade propylene (PGP) was under research focus in the last years. In our previous work (10), we have employed a single five-step VPSA process including, feed, co-current rinse with propylene, co-current intermediate depressurization, counter-current evacuation, and co-current pressurization with feed. Several experiments were performed, basically aiming to improve the performance of the process in terms of propylene purity and recovery. An important issue to be also taken into account is power consumption; since propylene is the most adsorbed compound it should be purified using a vacuum. Using extremely low pressures result in high power consumption. In our previous studies using zeolite 4A with crystal radius of 1.9 μm, we have employed 10 kPa as the evacuation pressure, but using this value, the power consumption is significant (10). For this reason, we have analyzed the process performance keeping zeolite crystal radius constant and using different evacuation pressures. The results are shown in Fig. 1. It can be observed that reducing the evacuation pressure, the propylene recovery increases almost linearly. However, the purity decreases sharply for pressures of 10 kPa and smaller. Using pressures higher than 10 kPa, the adsorption/desorption

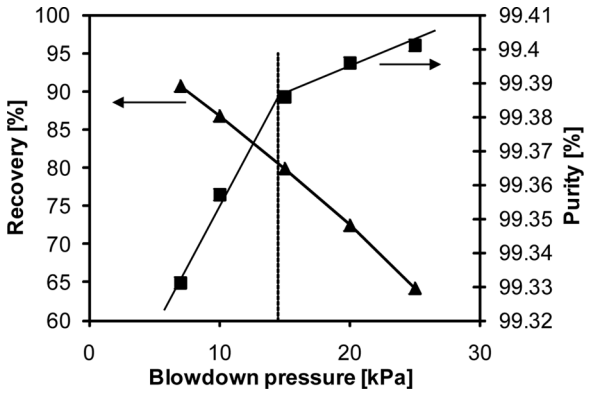

FIG. 1. Effect of evacuation pressure in the performance of front VPSA unit for propane – propylene separation using zeolite 4A with 1.9 μm crystal radius at 433 K. Symbols: ■ propylene purity [%]; ▲ recovery [%].

TABLE 2
Adsorption equilibrium and kinetic parameters of propane and propylene in zeolite 4A

	q_m (mol/kg)	K_i^o [kPa^{-1}]	$-\Delta H$ [kJ/mol]	a_i	D_p [m^2/s]*	D_c [m^2/s]*
C_3H_6	2.600	8.44×10^{-6}	28.2	2.612	8.0×10^{-6}	6.1×10^{-16}
C_3H_8	3.103	2.81×10^{-5}	15.6	2.189	8.1×10^{-6}	2.7×10^{-18}

*Values at 423 K.

of propane within each VPSA cycle is negligible. However, when the pressure is decreased further, we are increasing the driving force to desorb propane which results in decreases of propylene purity in the order of 0.1%. For this reason we have fixed 15 kPa as the evacuation pressure in this study. It can be concluded that there is a significant drop in propylene recovery if pressure is higher than 15 kPa, the reason why we have fixed this value for this study. The column properties and the simulation parameters are detailed in Table 2.

The design of this VPSA process is complex since we are intending to purify the most adsorbed compound to a very high purity, keeping recovery as high as possible. However, this is difficult since we employ a kinetic adsorbent with strong diffusional resistances and where the mass transfer zone is larger than the bed length. The other variable that affects process performance is temperature within the column. The process is operated under adiabatic conditions, so temperature variations of 20 K over the cycle are expected, especially in the initial part of the bed. The cycle design of the front VPSA has included different possible configurations using the following steps:

- Feed: Step where selective adsorption of propylene takes place at the highest pressure of the cycle, P_{feed}.
- Co-current depressurization: The pressure of the column is reduced to an intermediate pressure, P_{inter}. The stream exiting the column can be used to pressurize another column after evacuation (pressure equalization).
- Rinse: A stream containing purified propylene is employed to displace propane from the gas phase to enrich the molar fraction of propylene. In zeolite 4A the adsorption of propane is very slow, and most of the propane is removed from the gas phase.
- Co-current second depressurization: The objective of this step is to remove the rest of the propane existing in the column. For this purpose, the rinse step should be incomplete; otherwise, massive amounts of propylene are lost. To save compression energy, the outlet stream should be applied for pressure equalization.
- Counter-current evacuation: In this step, the adsorbent is partially regenerated and propylene is recovered as product. The lowest pressure of the cycle, P_{blow}, is reached. Recompressing the propylene product causes a major share of power consumption of the process.
- Pressure equalization(s): The streams taken from one column from the previous two depressurization stages can be recycled to other column to reduce compression energy.
- Counter-current purge: Additional regeneration of the adsorbent and reduction of C_3H_6 partial pressure in the gas phase can be also achieved by purging with propane. The objective of the purge step is to reduce propylene losses in the subsequent feed step.
- Co-current Pressurization: The pressure is increased to start a new cycle. This step is performed with the feed stream.

The sensitivity of process performance (purity, recovery) for various process parameters is shown in Table 3. Only the most important parameters were considered in this analysis: temperature, crystal radius of zeolite crystal, and pressures of different steps. The amount of gas employed in the rinse step is important to remove propylene from the column. The amount of gas can be significantly reduced if the rinse is performed at an intermediate pressure. If the rinse step

TABLE 3
Operating conditions for simulations performed to scale-up the front VPSA process using zeolite 4A according to initial assumptions

Column length [m]	6.50
Column radius [m]	1.72
Column porosity	0.40
Adsorbent bulk density [kg/m^3]	758.0
Pellet radius [m]	8×10^{-4}
Overall heat coef. [W/m^2K]	0.00
Temperature [K]	433
Pellet density [kg/m^3]	1210
Pellet porosity	0.34
Propane in feed [mol/mol]	0.60
Propylene in feed [mol/mol]	0.40
Propylene in rinse [mol/mol]	1.00

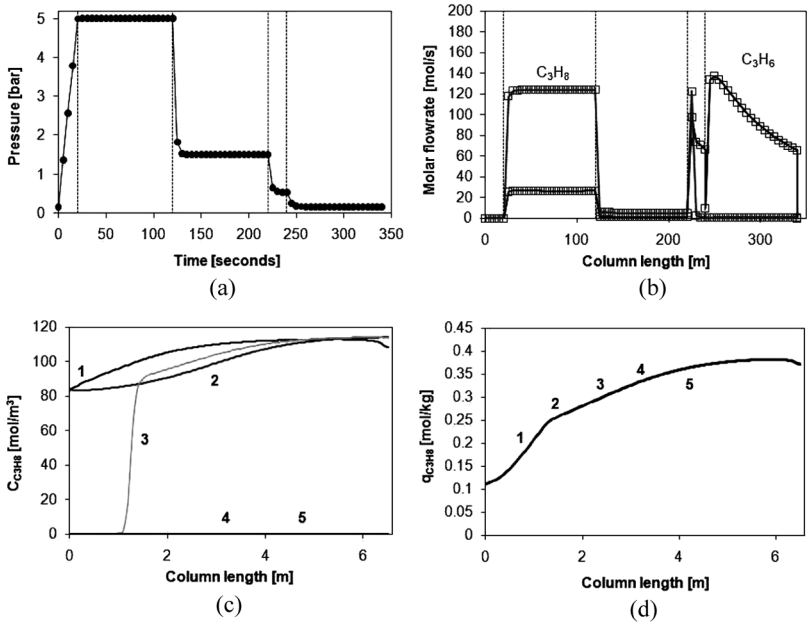

FIG. 2. Simulated results from front VPSA process for C_3 separation using zeolite 4A when cyclic steady state was reached. (a) pressure history of one cycle; (b) propane and propylene molar flowrate outlets; (c) C_3H_8 gas concentration and (d) C_3H_8 amount adsorbed at the end of each step. Number corresponds to the values at the end of each step 1: pressurization; 2: feed; 3: rinse; 4: depressurization; 5: evacuation.

is performed at the same pressure as the feed step, the partial pressure of propylene increases from 200 kPa in feed step to almost 500 kPa in rinse step and thus, too much propylene is adsorbed in the bed instead of removing the propane. Another important variable is the pressure of the second depressurization step. This pressure is critical to reduce the amount of propane in the column prior to evacuation. If we use higher pressures, the amount of propane that remains in the column is enough to contaminate the purity to values around 98%. We have used purified propylene in the simulations to reduce computational time. We have also made simulations with 99.4% of propylene in the rinse step observing only minor changes in the propylene purity. This cycle can accommodate small amounts of propane in the rinse step provided that the depressurization pressure can be adjusted to remove it from the gas phase.

Another important conclusion regards the application of a purge step. To attain a significant gain in propylene recovery, large propane quantities would be required for purging at low pressures. As this has proven to be inefficient, a purge step is not used in this VPSA unit.

The crystal size of zeolite 4A is very important to regulate the propylene purity. We have previously shown that using larger crystals we can increase the purity of propylene at the expense of recovery (25). Using larger crystals, the amount of propylene adsorbed can dilute easily the propane in the gas phase, increasing the overall purity of the recovered propylene. We have increased the radius of the zeolite crystals to 2.2 μm and achieved a purity of more than 99.5%. An example of the internal profiles of propane and propylene is shown in Fig. 2 (corresponding to the results of simulation 4 in Table 3). In Fig. 2a it can be observed that a large amount of propylene is lost in the feed step, the reason why recovery from this front VPSA unit is not large. On the other side, in Fig. 2d we can see that the concentration of propane after the second depressurization is very small. Another interesting feature of this process is that the amount adsorbed of propane is almost constant within the entire cycle. The plots shown in Fig. 2 show the behavior of the process after the cyclic steady state is reached, after more than 200 cycles. After the first cycles, once temperature profiles are developed, the change

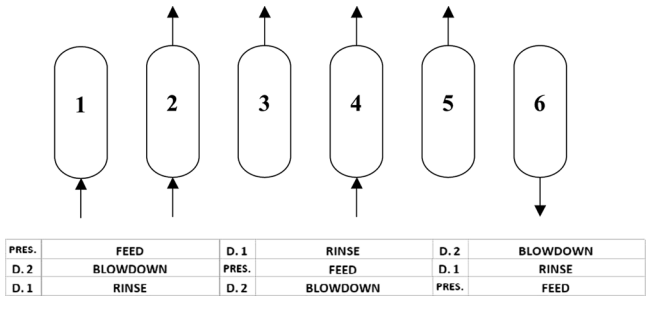

FIG. 3. Front VPSA cycle scheme and step scheduling to produce polymer-grade propylene. Steps are: (1) pressurization, (2) feed, (3) depressurization 1, (4) rinse, (5) depressurization 2 and (6) evacuation.

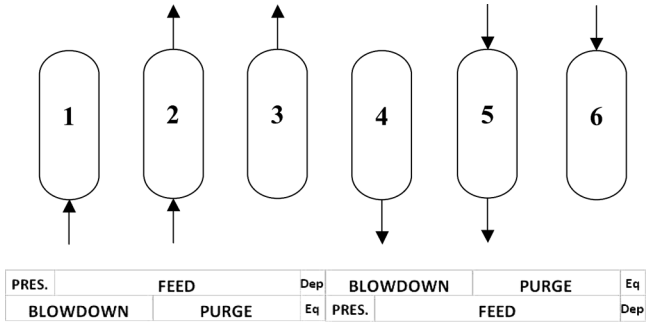

FIG. 4. VPSA cycle scheme and step scheduling of the tail unit to recover propylene. Steps are: (1) pressurization, (2) feed, (3) depressurization, (4) evacuation, (5) purge and (6) pressure equalization.

in the other parameters is extremely small, but a significant change in purity is observed (from 99.9 to 99.6%). These changes occur until the propane load in the adsorbent attains a stable value.

The scheme and scheduling of the process steps in the front VPSA unit is detailed in Fig. 3. The 3-column array scheduling was developed for continuous processing of feed.

Table 3 shows a set of operating conditions to produce polymer grade propylene. Unfortunately, the losses of propylene in the stream exiting the feed step are significant and the total propylene recovery is lower than 60%. Since our objective is to obtain both high purity and high recovery, we use a second "tail" VPSA unit that recovers propylene.

INCREASING PROPYLENE RECOVERY: TAIL VPSA UNIT

The objective of this unit is to recover propylene from the propane stream exiting the feed step of the front unit. The recovered propylene is recycled to the feed step of the front unit. For this reason, we have designed this unit to produce propylene with purity close to the feed composition (40% propylene). The purity of propylene was fixed to 40% only as reference to design the front VPSA with a fixed feed composition. However, increasing the purity of the recovered propylene may results in compression energy savings.

This unit does not need to operate with kinetic adsorbents where the mass transfer zones are large and thus the unit productivity is reduced. In this case, we want a fast propylene adsorption. Additionally, we do not want to lose propylene so a purge step is necessary. Since the requirements of this unit are completely different from the front VPSA unit, other design concepts are discussed.

The first modification concerns the adsorbent to be employed. We can select (from the existing database of commercial adsorbents) a proper adsorbent to replace zeolite 4A or we can choose conditions where diffusion of propylene in zeolite 4A is fast enough to be considered attractive. In order to keep a basis for comparison (same thermodynamic equilibrium and diffusion constants), we have reduced the crystal radius of the zeolite 4A to 0.3 μm. A reduction in crystal size has a direct impact in the time constant for diffusion in micropores. The ratio of micropore/macropore diffusion rates is given by:

$$R = \frac{15KD_c}{r_c^2} \Big/ \frac{8D_p}{R_p^2} \qquad (1)$$

TABLE 4
Front VPSA simulations of propane-propylene separation employing zeolite 4A[+]

N°	T [K]	t_{blow} [s]	t_{purge} [s]	P_{depr} [kPa]	P_{rinse} [kPa]	P_{blow} [kPa]	Q_{rinse} [SLPM]°	Q_{purge} [SLPM]°	r_c [μm]	Purity [%]	Recovery [%]
2	433	100	0	50	500	10	39412.9	0	1.9	97.02	69.03
3	433	100	0	100	500	10	59119.4	0	1.9	98.08	66.23
4	433	100	0	50	500	10	59119.4	0	1.9	99.35	56.41
5	433	100	0	50	250	10	29559.7	0	1.9	98.60	66.53
6	433	100	10	50	150	10	19706.5	3547.2	1.9	99.36	64.97
7	433	100	10	50	150	10	14779.9	3547.2	1.9	99.32	64.67
8	433	100	10	50	150	10	14779.9	3547.2	1.9	98.08	69.40
9	433	100	10	50	150	15	19706.5	3547.2	1.9	99.36	62.00
10	423	100	10	50	150	15	19706.5	3547.2	2.2	99.54	58.93
11	423	100	10	70	150	15	19706.5	3547.2	2.2	98.28	62.81
12	423	90	10	50	150	15	19706.5	3547.2	2.2	99.57	56.88
14	423	100	0	50	150	15	19706.5	0	2.2	99.56	59.42

°SLPM: Standard liters (1 bar, 298 K) per minute.
[+]In all runs: Pressurizatin time: 20 s; Feed time: 100 s; Rinse time: 100 s; Depressurization time: 20 s; $Q_{feed} = Q_{press}$: 295597 SLPM.

If $R < 0.1$, then the control is within the micropores. If $R > 10$ is within the macropores and if $0.1 < R < 10$ then there is a mixed control. In this work, in the larger zeolite crystals (used in the front VPSA), $R = 5.8 \times 10^{-3}$ while for the smaller zeolite crystals (0.3 μm used in the tail VPSA) is $R = 0.31$.

The tail unit is solely a recovery process so it is expected to use less power than the front VPSA. It is also expected to yield higher unit productivities. For this reason we have used a simplified design. A two-column unit operating with a modified Skarstrom cycle (including pressure equalization) is employed. The scheme of the process steps and its scheduling is shown in Fig. 4. The scheduling of this 2-column unit is not continuous, reason why a tank is required to regulate a constant flowrate as feed without accumulation of gas coming from the first process. In this unit, the streams leaving steps 4 and 5 are recycled to the first VPSA unit. The two columns have 7.5 m height and 3.0 m diameter. To reduce the power consumption, our initial simulations considered evacuation at 100 kPa, but almost no propylene was desorbed under those conditions, reason why it was reduced. The operating conditions of the tail VPSA unit are detailed in Table 4 while the results are shown in Table 5.

The effect of operating conditions was also evaluated in this unit. We have modified the column diameter, the purge flowrate, and also the evacuation and purge pressure. We have observed that the most important operating condition is again directly related to power consumption; the pressure of the evacuation step determines propylene desorption. All other operating conditions have minor effects when compared to the evacuation and purge pressure.

The key conclusion is that the tail unit (two columns, 53 m^3 each) is smaller than the front PSA unit (three columns, 60 m^3 each); however, the size of both units is in the same order of magnitude. A propylene purity of 40% results in a high recycle rate from the tail to the front unit, with significant costs of power for recompression.

TABLE 5
Operating conditions for tail VPSA process using zeolite 4A

Propane molar fraction	0.8224
Propylene molar fraction	0.1776
Temperature [K]	423
Inlet pressure [kPa]	500
Total feed flow [mol/s]	152
Pellet density [kg/m^3]	1210
Pellet porosity	0.34
Pellet radius [m]	8×10^{-4}
Crystal radius [μm]	0.3
Overall heat coefficient [W/m^2K]	0.00

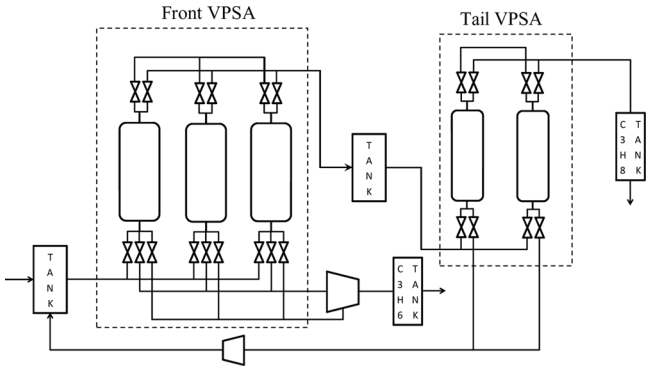

FIG. 5. Simplified scheme of the dual VPSA configuration to produce polymer grade propylene using zeolite 4A.

PROCESS INTEGRATION

The final objective of this work is to design an alternative adsorption-based process for separation of propane–propylene mixtures. Once we have designed a process that is able to obtain PGP propylene (front VPSA) and a second process to recover C_3H_6 (tail VPSA), we have to integrate these units. According to the cycles employed in both VPSA units, a possible flowsheet is shown in Fig. 5. This design considers that the flowrate in most of the steps will not be constant and thus, several tanks are associated to these processes. Associated with the flowsheet, in Fig. 6 we present the mass balance of the complete C_3-separation unit, showing how we have achieved the desired propylene purity and recovery.

The last step of the process integration was to compare the volume of the columns and the power consumption with distillation (Table 6). The adsorbent volume in the two VPSA units is 287 m^3, distributed in 181 m^3 in the front VPSA unit and 106 m^3 in the tail VPSA. The volume required to process the propane–propylene stream is significantly smaller than the volume of a C_3 splitter (621 m^3) estimated for the same purpose. The flowsheet used for the estimation of power consumption by distillation is shown in Fig. 7. The power consumption of the two-stage VPSA

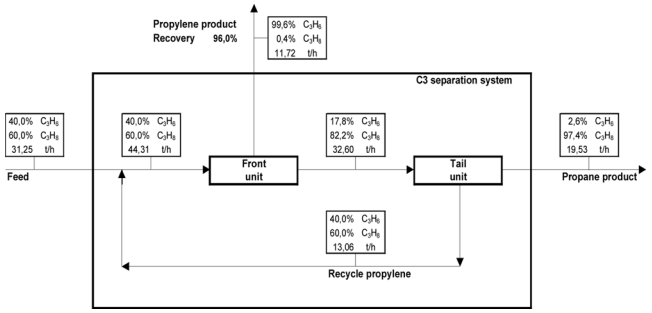

FIG. 6. Mass balance of the two VPSA processes to produce polymer grade propylene using zeolite 4A.

TABLE 6
Tail VPSA simulations of propane-propylene separation employing zeolite 4A[+]

N°	R_c [m]	L_c [m]	t_{blow} [s]	t_{purge} [s]	P_{depr} [kPa]	P_{blow} [kPa]	Q_{purge} [SLPM]	Purity C_3H_8 [%]	Purity C_3H_6 [%]	Recovery C_3H_6 [%]	Recovery C_3H_8 [%]
1	1.5	7.5	60	50	250	20	17888.3	97.53	41.72	89.32	59.73
2	1.5	7.5	60	55	250	20	35776.6	97.93	41.05	90.31	59.01
3	1.5	7.5	60	60	250	20	35776.6	98.24	40.66	91.82	58.24
4	1.5	7.5	60	60	250	30	35776.6	97.47	40.73	88.82	59.21
5	1.4	7.5	70	60	280	30	25554.7	96.95	42.68	86.81	63.70
6	1.3	7.5	70	30	280	15	25554.7	97.41	44.76	88.79	66.47

[+]Equalization time was in all the simulations $t_{eq} = 10$ seconds. Feed time was also fixed in $t_{feed} = 100$ seconds. Feed pressure was 500 kPa.

TABLE 7
Comparison of distillation and dual VPSA process performance

	Distillation	VPSA
Propylene purity [%]	99.5	99.6
Propylene recovery [%]	95.6	95.9
Separation volume [m^3]	611 (3.6 m × 60 m)	287*
Power consumption [MW]	3.22°	3.82[+]

*The total separation volume corresponds to 181 m^3 of the front VPSA unit and 106 m^3 of the tail unit.
°Electrical power for vapor compression.
[+]Power consumption is divided in: 0.59 MW feed compression; 2.33 MW front VPSA; 0.90 MW tail VPSA.

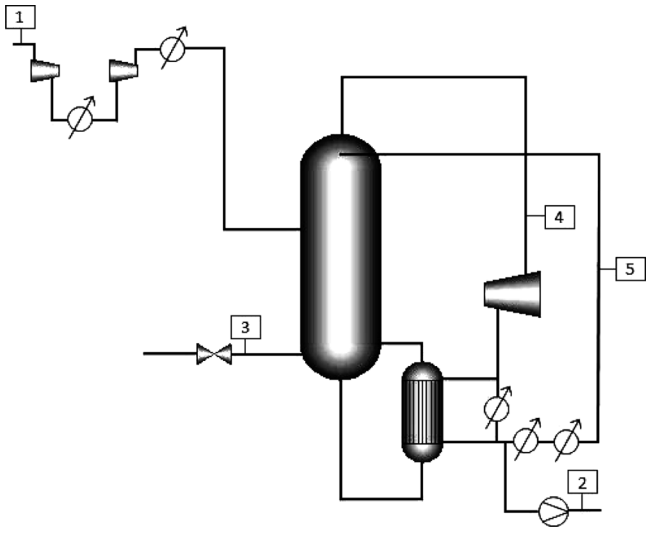

FIG. 7. Flowsheet of C_3 distillation used for power consumption calculations.

configuration is higher than for distillation, mainly due to the low evacuation pressures. The main source of power consumption is the front VPSA process where the evacuation pressure is rather low and flowrates are large.

This work shows that the two VPSA units in series can be used to produce polymer grade propylene using available kinetic adsorbents (e.g., zeolite 4A). Significant savings in power consumption could be achieved if adsorbents with more linear isotherms are found, as the evacuation could be performed at higher pressure.

This work reports a methodology to achieve polymer grade propylene coupled with propylene recovery over 94%. However, several actions are required to bring this process to commercial scale. Process optimization, particularly regarding the tail VPSA unit, is perhaps the major challenge. The other issue that should be evaluated is the presence of contaminants in the ppm level, namely ethane and acetylene. The strong adsorption of acetylene in zeolites may result in contamination of the product or in zeolite deactivation.

CONCLUSIONS

We have evaluated the use of Vacuum Pressure Swing Adsorption (VPSA) to produce polymer grade propylene (PGP) using zeolite 4A. The 3-column front VPSA unit operates with a new scheduling consisting on the following steps: feed, depressurization, rinse with purified propylene, second depressurization, evacuation, pressure equalization, and pressurization with feed. The process simulation predicts a propylene purity of 99.6% and a recovery of 67%. In order to improve recovery, we have employed an additional VPSA tail unit. Zeolite 4A with small crystal radius is used in order to reduce the kinetic limitations and approach equilibrium much faster. The tail unit has two columns with a modified Skarstrom cycle (feed, depressurization, evacuation, purge, pressure equalization, and pressurization) and yields propylene with purity of

40% that is recycled to the first VPSA unit. Using this dual VPSA concept, the volume of separation could be clearly reduced when compared to distillation. However, the power consumption of this process is somewhat higher indicating that more research is required to improve this alternative process. Future efforts should focus on minimizing power consumption. New adsorbents with more linear isotherms could facilitate this approach.

REFERENCES

1. Eldridge, R.B. (1993) Olefin/paraffin separation technology: A review. *Ind. Eng. Chem. Res.*, 32: 2208–2212.
2. Ren, T.; Patel, M.; Blok, K. (2004). Energy Efficiency and Innovative Emerging Technologies for Olefin Production. Proceedings of the European Conference on Energy Efficiency in IPPC Installations, Vienna, Austria, 21–22 October, 2004.
3. Mersmann, A.; Fill, B.; Hartmann, R.; Maurer, S. (2000) The potential of energy saving by gas phase adsorption processes. *Chem. Eng. Technol.*, 23: 937–944.
4. Eldridge, R.B.; Siebert, F.A.; Robinson, S. Hybrid separations/distillation technology. Research opportunities for energy and emissions reduction. Available at: http://www1.eere.energy.gov/industry/chemicals/pdfs/hybrid_separation.pdf. Last accessed April 2009.
5. Giannakopoulos, I.G.; Nikolakis, V. (2007) Recovery of hydrocarbons from mixtures containing C_3H_6, C_3H_8 and N_2 using NaX membranes. *J. Membrane Sci.*, 305: 332–337.
6. Da Silva, F.A. (1999). *Cyclic Adsorption Processes: Application to Propane/Propylene Separation*. Ph.D. Thesis Faculty of Engineering, University of Porto.
7. Cheng, L.S.; Wilson, S.T. (2001). Vacuum Swing Adsorption Process for Separating Propylene from Propane. U.S. Patent 6,296,688.
8. Yang, R.T.; Padin, J.; Rege, S.U. (2001). Selective Adsorption of Alkenes Using Supported Metal Compounds. U.S. Patent 6,423,881.
9. Bryan, P.F. (2004) Removal of propylene from fuel-grade propane. *Sep. Purif. Rev.*, 33: 157–182.
10. Grande, C.A.; Rodrigues, A.E. (2005) Propane-propylene separation by pressure swing adsorption using zeolite 4A. *Ind. Eng. Chem. Res.*, 44: 8815–8829.
11. Ruthven, D.M.; Reyes, S.C. (2007) Adsorptive separation of light olefins from paraffins. *Microporous Mesop. Materials.*, 104: 59–66.
12. Al-Muhtaseb, S.A. (2008) Role of catalyst type in the selective separation of olefinic and paraffinic hydrocarbons using xerogel-based adsorbents. *Carbon.*, 46: 1003–1009.
13. Järvelin, H.; Fair, J.R. (1993) Adsorptive separation of propane–propylene mixtures. *Ind. Eng. Chem. Res.*, 32: 2201–2207.
14. Ramachandran, R.; Dao, L.H.; Brooks, B. (1994). Method of Producing Unsaturated Hydrocarbons and Separating the Same from Saturated Hydrocarbons, U.S. Patent 5,365,011.
15. Da Silva, F.A.; Rodrigues, A.E. (2001) Vacuum swing adsorption for propylene/propane separation with 4A zeolite pellets. *Ind. Eng. Chem. Res.*, 40: 5758–5774.
16. Da Silva, F.A.; Rodrigues, A.E. (2001) Propylene/propane separation by VSA using commercial 13X zeolite pellets. *AIChE Journal.*, 47: 341–357.
17. Grande, C.A.; Firpo, N.; Basaldella, E.; Rodrigues, A.E. (2005) Propane/propylene separation by SBA-15 and π-complexated Ag-SBA-15. *Adsorption*, 11: 775–780.
18. Padin, J.; Rege, S.U.; Yang, R.T.; Cheng, L.S. (2000) Molecular-sieve sorbents for kinetic separation of propane/propylene. *Chem. Eng. Sci.*, 55: 4525–4535.
19. Cho, S.H.; Han, S.S.; Kim, J.N.; Choudary, N.V.; Kumar, P.; Bhat, S.G.T. (2001). Adsorbents, Method for the Preparation and Method for the Separation of Unsaturated Hydrocarbons for Gas Mixtures. U.S. Patent 6,315,816.
20. Olson, D.H. (2002). Light Hydrocarbon Separation Using 8-Member Ring Zeolites. U.S. Patent 6,488,741.
21. Kuznicki, S.M.; Bell, V.A. (2003). Olefin Separation Employing ETS Molecular Sieves. U.S. Patent 6,517,611.
22. Reyes, S.; Krishnan, V.V.; De Martin, G.J.; Sinfelt, J.H.; Strohmaier, K.G.; Santiesteban, J.G. (2003). Separation of Propylene from Hydrocarbon Mixtures. International Patent WO 03/080548 A1.
23. Grande, C.A.; Rodrigues, A.E. (2004) Adsorption kinetics of propane and propylene in zeolite 4A. *Chem. Eng. Res. & Design.*, 82: 1604–1612.
24. Yang, R.T. (2003) *Adsorbents. Fundamentals and Applications*; J. Wiley: New Jersey.
25. Grande, C.A.; Basaldella, E.I.; Rodrigues, A.E. (2004) Crystal size effect in vacuum pressure swing adsorption for propane/propylene adsorption. *Ind. Eng. Chem. Res.*, 43: 7557–7565.
26. Grande, C.A.; Gigola, C.E.; Rodrigues, A.E. (2004) Propane–propylene binary adsorption on zeolite 4A. *Adsorption.*, 9: 321–329.