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Air Products and Chemicals, Inc.

Organization

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FINAL PROJECT REPORT

Project Title: "Development of New Pressure Swing Adsorption Technology to Recover High Valued Products from Chemical Plant Refinery Waste Streams"

Covering Period: March 15, 2000 through March 14, 2004

Date of Report: June 14, 2004

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Summary

Air Products successfully concluded the High Performance PSA Project on 14 March 2004. The Phase I technology for converting the waste gas from polyolefin production units into products useful for recycle is currently operating in two commercial facilities. The commercial implementation of the monomer recovery technology covers two major segments for the market. One commercial unit recovers off-gas from a new, world-scale, single-train polyethylene unit. The second commercial unit recovers combined waste gas from up to seven individual trains, producing polypropylene within a single site. These two units recover approximately 14 MMlb/yr of olefin monomer and 33 MMlb/yr of nitrogen, resulting in an energy savings to the nation of 6580 MMSCFY of natural gas and 3192 MWh of electric power. Performance testing under Task 3 shows that the PSA units are operating stably, and the customers are very pleased with the systems.

Research- and pilot-scale process development on the technology for recovering H₂ from refinery off-gas (ROG) streams (Phase II) also demonstrated very good results. Adsorbent materials that are resistant to the cyclic and aromatic compounds often found in these off-gases were identified and characterized. However, market forces intervened to prevent a commercial demonstration of the technology.

The clean fuels initiative has created a very large demand for additional hydrogen for refiners. Unfortunately, this demand is so large that most often the modest amount of hydrogen available for recovery is eclipsed by the new requirement. The most economic choice for the refiners is to add substantial on-purpose hydrogen generation capacity to meet the new demand and ignore the incremental contribution available from PSA ROG H₂ recovery for now. We could not expect a refiner to consider recovering the additional ROG H₂ for at least 5 years. Refiners were not interested in hosting a demonstration of the ROG PSA technology. Moreover, the expected delay in opening the market for ROG H₂ PSA opportunities caused Air Products to exit the market. Therefore, the ROG H₂ PSA demonstration was never executed. The ROG H₂ PSA program ended after completion of the adsorbent material research and pilot-scale process experiments.

Task 1: Acquire Basic Material Property Data

Phase I and Phase II: Adsorbent Material Property Data

Table 1 provides a list of the various adsorption isotherms measured in support of the Monomer Recovery/ROG H₂ PSA program. Isotherms were measured at two adsorption temperatures (30 and 70°C) so that heats of adsorption could be derived. For gaseous components, isotherms were measured in a standard volumetric adsorption apparatus. For liquids (pentane and higher), isotherms were measured in a McBain balance.

Table 1. Adsorption isotherms

Adsorbent	H ₂	C1	C2	C3	C4	C5	C6	C7(toluene)	C8	H ₂ S
Coconut-shell carbon	X	X	X	X	X	X	X	X	X	X
Coal-based carbon	X	X	X	X	X					
Large-pore carbon	X	X						X		
5A zeolite	X	X	X	X	X					
Activated alumina	X	X	X	X	X	X	X	X	X	X
Base-treated alumina	X	X						X		X
Small-pore silica gel	X	X	X	X	X	X	X	X	X	X
Wide-pore silica gel	X	X	X	X	X			X		
Water-stable silica gel	X	X			X					
Hydrotalcite				X	X	X	X			
Titania				X	X	X	X			

Adsorbents with High CH₄/H₂ Selectivity

In order to produce high-purity H₂ from ROG feed gases, the final adsorbent layer in the PSA must have: 1) good CH₄ capacity and 2) good CH₄/H₂ selectivity. Adsorbents with these properties should be microporous materials like activated carbons and zeolites. Table 2 provides the Henry's law constant (initial isotherm slope) for CH₄ and H₂ adsorption at 30°C, the CH₄/H₂ selectivity and isothermal CH₄ working capacity between 3 and 0.5 atm.

Table 2. Henry's Law constants

Adsorbent	(mmole/g/atm) K CH ₄	(mmole/g/atm) K H ₂	S CH ₄ /H ₂	(mmole/cc) CH ₄ working capacity
Coconut carbon	2.1	0.036	58.3	0.67
Coal carbon	0.75	0.022	34.1	0.60
5A zeolite	1.1	0.029	37.9	0.58
Silica gel	0.12	0.0084	14.3	0.20
Activated alumina	0.060	0.0046	13.0	0.12

From the results in Table 2, it is clear that silica gel and alumina are not optimal adsorbents for CH₄ removal from H₂. The microporous carbons and zeolite have much improved CH₄/H₂ selectivity and CH₄ working capacity. Of the microporous adsorbents tested, the coconut shell carbon had the highest CH₄/H₂ selectivity and the highest CH₄ volumetric working capacity (mmole/cc of bed). The results in Table 2 suggest that coconut shell-based carbon is the preferred CH₄ removal adsorbent from an equilibrium standpoint.

The equilibrium and mass transfer data collected indicate that coconut-shell-based, activated carbon is the preferred material tested for CH₄ removal from H₂, i.e., the final adsorbent layer in an ROG H₂ PSA.

Adsorbents for Removal of C₂-C₆ Hydrocarbons

Microporous adsorbents like activated carbon are preferred for CH₄ removal from H₂. However, as the molecular weight of the hydrocarbon increases, it becomes more strongly adsorbed. Figure 1 shows the ethane, propane and butane isotherms on coconut-shell carbon at 30°C.

Figure 1. Ethane, propane and butane isotherms at 30°C on coconut shell carbon

Clearly, butane is much more strongly adsorbed on the material than is propane or ethane. The strength of butane adsorption makes its desorption in a PSA process difficult. For coconut-shell carbon at 30°C and between 1 and 0.1 atm, the volumetric isothermal working capacities for ethane, propane and butane are 1.0, 0.5 and 0.2 mmole/cc of bed, respectively. This low working capacity and high Henry's law constant for butane adsorption on coconut-shell carbons suggests that adsorbents other than microporous activated carbon are preferred for C₄₊ removal from H₂.

Figure 2 shows the butane and hexane isotherms on small-pore silica gel (surface area = 750 m²/g) and activated alumina (320 m²/g). The butane volumetric working capacity between 1 and 0.1 atm is 1.6 and 0.8 mmole/cc of bed for silica gel and alumina, respectively. Clearly, the volumetric butane working capacity is higher for silica gel than for alumina.

Figure 2. Butane and hexane adsorption isotherms at 30°C on silica gel and alumina

Figure 2 shows hexane isotherms for silica gel and alumina ranging from 0.1 to 0.01 atm. The volumetric working capacities for silica gel and alumina are 1.8 and 0.9 mmole/cc of bed, respectively. Again, silica gel appears to be the preferred material for C₄ to C₆ removal from H₂ in a PSA process.

Removal of C₆₊ Hydrocarbons

Figure 3 shows toluene adsorption isotherms at 30°C on alumina, base-treated alumina, small-pore silica gel and wide-pore silica gel. The isothermal volumetric toluene working capacities between P/P₀ of 0.5 to 0.1 for wide-pore gel, small-pore gel, base-treated alumina and alumina are 0.55, 0.30, 1.2 and 2.8 mmole/cc of bed, respectively. This result clearly shows that for aromatics removal, alumina-based materials are preferred over silica gels. In addition, small-pore gels are water sensitive (exhibit particle breakage on contact with liquid water). Thus, an initial alumina-based adsorbent layer for water and aromatics is a good guard bed for the C₄-C₆ removal silica gel layer. A large-pore carbon was also tested, but its toluene working capacity was only 0.35 mmole/cc.

Figure 3. Toluene isotherms at 30°C

In summary, equilibrium properties suggest that the preferred adsorbent arrangement for an ROG H₂ PSA is a first layer of alumina for water and aromatics removal, followed by a layer of small pore silica gel for C₆-C₄ removal and a final layer of coconut shell carbon for C₃-C₁ removal. The optimum proportions of each layer are given in US 6,483,001.

Kinetic Performance of Adsorbents

Breakthrough curves were developed for numerous adsorbate/adsorbent pairs of interest for ROG H₂ PSA. The column used in this study was 1 inch in diameter, and the column length varied from 1 to 6 feet. The breakthrough data was used to derive mass transfer coefficients for model simulations. Table 3 gives a list of breakthrough curves measured. The feed concentrations were 0.1% in H₂ for methane and ethane and 0.05% in H₂ for all other hydrocarbons. Low inlet concentrations were used to avoid significant heat-up during breakthrough measurements.

Table 3. Measured breakthrough curves

Adsorbent	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	toluene	(psig) Feed P	(lbmoles/hr/ft ²) Feed flow rate
Coconut carbon, 6x12 mesh	X	X	X	X	X			250	40,26
Coal-based carbon, 2 mm	X	X	X	X				250	26
Activated alumina, 7x14 mesh	X	X	X	X	X	X	X	250, 350	70,26
Base-treat alumina, 7x14 mesh							X	250	40
Small pore silica gel, 6x16 mesh	X	X	X	X	X	X	X	250, 350	40,26
5A zeolite, 1/16" extrudate	X							250	26
Water stable silica gel, 8x12 mesh						X		350	40

Adsorbents with High CH₄/H₂ Selectivity

Adsorbents in the final layer (product end) of the H₂ PSA should have good mass transfer for CH₄ adsorption, since high-purity H₂ is required (10-1000 ppm CH₄). Breakthrough curves for dilute CH₄ removal (0.1%) from H₂ were carried out at 25°C and a feed flow rate of 40 lbmoles/hr/ft² cross sectional. The CH₄ mass transfer zone lengths were about 50 inches for the same particle size of the coconut-shell carbon, the 5A zeolite and the coal-based carbon. This result suggests that equilibrium performance is most important for CH₄ removal from H₂ for equal size particles of activated carbon and zeolite.

Adsorbents for Removal of C₄-C₆ Hydrocarbons

Based on equilibrium measurements, it appears that small-pore silica gel is the preferred adsorbent for C₄-C₆ removal from H₂. Butane breakthrough curves on activated alumina and small-pore silica gel are shown in Figure 4. The feed temperature was 25°C, feed pressure was 250 psig, the feed flow rate was 26 lbmoles/hr/ft² and the column length was 1 foot.

Figure 4. Butane breakthrough curves on alumina and silica gel

Clearly, silica gel has higher butane capacity. Silica gel also has a longer mass transfer zone length (11.3 in vs 9.4 in). Given the shorter mass transfer zone for alumina, it is worthwhile to test alumina for butane removal in pilot PSA tests.

Removal of C₆₊ Hydrocarbons

Breakthrough curves were also obtained with alumina and silica gel for toluene adsorption. In both cases, the toluene mass transfer zone was very sharp, between 2 and 3 inches. Given alumina's lower Henry's Law constant for toluene, it appears to be the preferred adsorbent for toluene removal by PSA.

Adsorbent Stability

Experiments were conducted at the University of Kentucky Center of Applied Energy Research to look into the stability of various adsorbents with respect to various hydrocarbons. Stability tests were conducted in a TGA apparatus. Basically, the adsorbent of interest was exposed to dilute (500 to 1000 ppm) hydrocarbon in He for a given period at high pressure (15 atm). The sample pressure was then reduced to atmospheric, and a He purge was conducted. The P/F ratio investigated was 1.5 on an ACF basis, which is similar to that in a PSA process. This cycle was completed numerous times until a steady weight change on adsorption and purge was noted. After the steady-state weight change was noted, a purge at 100°C was carried out to determine if any hydrocarbon was irreversibly adsorbed.

Initial stability tests were conducted with coconut-shell activated carbon, activated alumina, base-treated alumina, small-pore silica gel and wide-pore silica gel and butane adsorption. With all adsorbents, it was determined that butane adsorbed during high-pressure feed could be totally desorbed by purging with He at ambient temperature. In the case of activated carbon, the He purge duration required for total butane desorption was 48 hours.

Subsequent adsorbent stability tests focused mainly on stability toward toluene, since this is a reactive component present in some ROG streams.

Figure 5. Toluene Cycles on Small Pore Silica Gel

The results in Figure 5 show that after 50 adsorption/desorption cycles, small-pore silica gel has not achieved a steady-state weight profile. Even after 50 cycles, the weight of toluene remaining on the silica gel is increasing. Figure 6 shows the same data, but with activated alumina. The alumina much more quickly achieves a constant weight profile. In addition, the delta weight change is greater than that for small-pore silica gel. The same type of behavior was noted with base-treated alumina.

Figure 6. Toluene Cycles on Activated Alumina

One final experiment was done to test the stability of adsorbents when adsorbing toluene. In this experiment, the adsorbent was exposed to 500 ppm toluene, 1 bar pressure and 70°C for 7 hours. The sample was then purged with He at 70°C to see if the original adsorbent weight could be recovered. Those results are presented in Figure 7.

The results in Figure 7 show that the large-pore gel, base-treated alumina and activated alumina maintained a constant weight during the seven-hour uptake period. The small-pore gel continued to adsorb toluene during this time frame. During the 300-minute He purge step, the large-pore gel, alumina and base-treated alumina regained their initial weight, indicating that all toluene adsorbed was desorbed, and no reaction took place on the adsorbent surface. The small-pore silica gel did not regain its original weight after 300 minutes of purge. However, by purging at higher temperature, all adsorbed toluene was desorbed, indicating that no surface reaction occurred with silica gel.

H₂S Adsorption

H₂S adsorption isotherms were measured on coconut-shell carbon, activated alumina, small-pore silica gel and base-treated alumina. In the case of activated carbon and silica gel, the adsorption isotherms were totally reversible. In the case of the alumina materials, H₂S did demonstrate some irreversible adsorption behavior. Stability tests in the TGA were conducted with coconut-shell carbon and small pore gel. Those tests showed that H₂S could be totally desorbed from carbon and silica gel at 70°C in He.

Figure 8. H₂S Adsorption at 30C

Adsorbent Characterization for Monomer Recovery

Table 4 provides a list of the adsorption isotherms measured in support of the monomer recovery program.

Table 4. List of measured isotherms

Adsorbent	N ₂	C ₂ H ₄	C ₃ H ₆	i-C ₄ H ₈
Coconut-shell carbon	X	X	X	X
Wood-based carbon	X	X	X	
Composite zeolite/alumina	X	X	X	
Small-pore silica gel	X	X	X	X
Activated alumina	X	X	X	X
5A zeolite	X	X		
Base-treated alumina	X	X		X

Table 5 gives isotherm data for the various materials tested, including Henry's law constants for N₂, C₂H₄ and C₃H₆, as well as olefin/N₂ selectivity and olefin volumetric isothermal working capacity between 2 and 0.5 atmospheres. All Henry's law constants are in units of mmole/g/atm at 30°C, and all working capacities are in units of mmole/cc of bed.

Table 5. Isotherm data for materials tested

Adsorbent	K N ₂	K C ₂ H ₄	K C ₃ H ₆	S C ₂ H ₄ /N ₂	S C ₃ H ₆ /N ₂	C ₂ H ₄ working capacity	C ₃ H ₆ working capacity
Coconut carbon	0.44	130	552	295	1255	0.45	0.36
Activated alumina	0.019	0.58	6.9	31	363	0.36	0.52
5A zeolite	0.62	156	-	252	-	0.13	-
Small pore silica gel	0.054	2.0	8.8	37	163	0.45	0.72
Base-treated alumina	0.016	0.53	-	33	-	0.24	-
Wood-based carbon	0.21	6.5	36.7	31	174	0.40	0.85
Alumina/zeolite composite	0.036	10	-	278	-	0.35	-

5A zeolite has a high C₂H₄/N₂ selectivity, but it owes its low isothermal working capacity to a very rectangular isotherm shape. Coconut-shell carbon and small-pore silica gel have the highest C₂H₄ isothermal working capacity. In addition, the selectivity of the carbon is better. However, for this application, the silica gel is the better material because its N₂ capacity is about 10 times less than that of the carbon. The low N₂ capacity of the adsorbent for this application is important to maintain a high N₂ recovery. If N₂ is strongly adsorbed, then significant amounts of N₂ will be lost in column blow-down steps. The alumina is also a good candidate because of its low N₂ capacity, reasonable selectivity and working capacity. Base-treatment of the alumina is not helpful. The zeolite/alumina composite has lower N₂ capacity than silica gel, but also a lower working capacity. Finally, the wood-based carbon is preferred over coconut materials for this application. The larger pores in the wood-derived material reduce N₂ capacity and improve the working capacity for C₃H₆ adsorption. Nonetheless, optimal materials for this application should have average pore diameters in excess of 2.0 nanometers (see EP 1302478) to optimize olefin working capacity and minimize N₂ adsorption.

Isobutylene Isotherms

Isobutylene is a potential impurity in various olefin recovery feed gas streams. Because isobutylene is strongly adsorbed and reactive, adsorbents used for this application should reversibly adsorb this component. Figure 9 shows the isobutylene isotherms at 30°C on small-pore silica gel and activated alumina. Both materials show reversible isobutylene adsorption and reasonable working capacity.

Figure 9. Isobutylene isotherms at 30°C

Kinetic Performance of Adsorbents

Breakthrough curves (Table 6) were completed on various adsorbent/adsorbate pairs of interest for the monomer recovery process and were carried out in the column previously described. All breakthrough curves were measured with 0.05% (500 ppm) of the impurity in He at 25°C feed temperature. The feed pressure was 250 or 350 psig, and the feed G-rate was 40 or 26 lbmoles/hr/ft². The breakthrough curves obtained were used to derive mass transfer coefficients needed for model simulations.

Table 6. Breakthrough curves measured

Adsorbent	C ₂ H ₄	C ₃ H ₆	i-C ₄ H ₁₀	Hexene
Coconut carbon	X		X	
Coal carbon	X			
Small-pore gel	X	X	X	X
Activated alumina	X	X	X	X

Figure 10 provides the C₂H₄ breakthrough curves on 8x14 mesh alumina, 6x16 mesh silica gel and 6x12 mesh carbon at a feed pressure of 250 psig and a feed G-rate of 26. Carbon had the highest capacity, as expected from isotherm measurements. The breakthrough on alumina was quite sharp, while the silica gel showed a higher C₂H₄ capacity than alumina, but a slightly longer mass transfer zone.

Figure 10. C₂H₄ breakthrough curves on alumina, silica gel and carbon

Adsorbent Stability

Adsorbents stability tests were conducted at the University of Kentucky Center of Applied Energy Research. In a high-pressure TGA unit, various adsorbents were exposed to high-pressure He containing 500 ppm C₂H₄, C₃H₆ and 1-hexene (an impurity in some monomer recovery streams). The samples were then depressurized to ambient pressure and purged with He. The experiments were conducted at purge/feed ratios of 1.5 (on an ACF basis) until a constant weight gain/loss profile was obtained. In the case of C₂H₄ and C₃H₆ adsorption, steady-state weight profiles were obtained with activated alumina, base-treated alumina, small-pore silica gel and coconut-shell carbon after a maximum of 50 adsorption/desorption cycles.

Experiments were then conducted with 1-hexene. Tests were completed with activated alumina, base-treated alumina and small-pore silica gel. For the three materials tested, only the base-treated alumina showed steady-state performance after 50 cycles. These results, shown in Figure 11, indicate that a pre-layer of base-treated alumina would be the best material for PSA removal of 1-hexene from monomer recovery feed streams.

Figure 11. 1-Hexene Cycles on base-treated alumina

Summary

1. A total of 12 different adsorbents and 13 different adsorbates were screened for equilibrium and mass transfer properties for application in monomer recovery PSA and ROG H₂ PSA. The data were used to derive equilibrium and mass transfer parameters required for computer model simulation of PSA processes.
2. The optimal adsorbent scheme for ROG H₂ PSA appears to be a 3-layer system. Optimal bed volumes of low-surface-area, intermediate-surface-area and high-surface-area adsorbents are given in US 6,483,001.
3. Activated alumina is the preferred feed end adsorbent in ROG H₂ PSA, owing to its stability toward liquid water and good PSA characteristics for aromatics adsorption.
4. Small-pore silica gel is the preferred adsorbent for C₄-C₆ hydrocarbon removal.
5. Coconut-shell-based, activated carbon is the preferred adsorbent for C₃-C₁ removal.
6. For monomer recovery PSA, alumina and silica gel are preferred adsorbents because of their low N₂ capacity, which results in high N₂ recovery.
7. Base-treated alumina is the preferred adsorbent for 1-hexene removal from monomer recovery feed gases.

Task 2: Process Development – Pilot-Scale Experiments

Phase I: Recovery of Hydrocarbons and Nitrogen from Polyolefin Plant Off-Gas

Experimental Pressure Swing Adsorption Setup

Two process development units for separation by adsorption were modified to collect data for the purification of nitrogen from the expected vent streams for slurry-phase polyethylene, gas-phase polyethylene, and gas-phase polypropylene processes. Each of the units was essentially the same in function and layout, except for the length of the adsorbent columns: 1-in.-OD x 10-ft-high columns (10-ft PDU); and 1-in.-OD x 20-ft-high columns (20-ft PDU). Figure 12 is a simplified schematic for a four-column cycle. All monomer recovery experiments were limited to four-column cycles.

Up to five gas streams were introduced by mass flow controllers and blended at 10 to 40 psig. These gases were heated to moderate temperatures to aid in the vaporization of liquid feed (butanes and heavier), which was metered to the gas stream by a liquid mass flow controller. The combined feed was then compressed up to 500 psig before introduction to the adsorbent columns through a common feed header. The heavier components were adsorbed on suitable materials, and the lighter component(s) broke through the column, creating a purified nitrogen product at high pressure. The column was then depressurized to as low a pressure as possible,

and the heavier components were purged from the bed by a stream enriched in the lighter components. In commercial installations, the pressure of this regeneration step is dictated by the downstream use of the adsorbed components. For monomer recovery, this is the inlet pressure of the feed compressor for the partial condensation equipment.

Pressure transmitters are located on all columns. Dry test meters measure the volume of product, blow-down, and purge gas. An IR analyzer, thermal conductivity detector, and on-line gas chromatograph measure the impurity level of the product. Data are collected when the system is at cyclic steady state and when the material balance error is <1%, often <0.5%. The cycle times are fixed in these experiments, and product purity is controlled by the total feed rate. The systems are automated for process control and data acquisition for continuous operation. Sample taps along one of the beds allow for the determination of axial concentration profiles.

Figure 12. Schematic for a Four-Column Cycle

Initial screening for this application was started with four-column cycles in the 10-ft PDU. The 10-ft PDU was first used to determine the expected performance for the purification of nitrogen from a feed stream typical of a partial condensation process for offgas from a slurry-phase polyethylene unit. Taking samples at one-foot intervals for gas chromatographic analysis provided axial concentration profiles. All other experiments were completed in the 20-ft PDU following an upgrade of the control and data acquisition system.

The adsorbent columns go through a series of steps with several column-to-column connections to maximize the efficiency of the separation. A schematic of the steps is illustrated in Figure 13, which shows the steps and column-to-column connections for the “4/1/2” cycle: 4 beds / 1 bed on feed / 2 steps of pressure equalization. The steps and column-to-column connections will be described in order for bed 1. All the other beds follow the same steps in order to provide a means for continuous production. In the first step (“feed”), the gas to be purified is introduced to

the feed end of bed 1, and the purified product is withdrawn from the product end. A portion of the product is returned to the system to pressurize bed 2, such that it reaches within 5 psi of the feed pressure before starting its feed step, which begins after the completion of the feed step for bed 1. The feed step continues until the impurity level in the product reaches the desired level. At this point, the feed gas is directed to bed 2, and the feed end of bed 1 is closed. The gas stored in bed 1 at the end of the feed step is then withdrawn from the product end (cocurrent to feed flow) and is used to pressurize and purge other columns. This cycle allows for higher recovery of the desired product contained within the column at the end of the feed step at high pressure.

Figure 13. Schematic of Process Steps

Bed																									
1	feed				eq1			pr	purge	eq2	blowdown				purge	eq2	eq1	repress							
2	eq1				repress				feed				eq1			pr	purge	eq2	blowdown				purge	eq2	
3	blowdown				purge	eq2	eq1				repress				feed				eq1			pr	purge	eq2	
4	eq1				pr	purge	eq2	blowdown				purge	eq2	eq1				repress				feed			

Purification of Nitrogen from Monomer Offgas Streams using PSA

Slurry Phase Polyethylene Process

The 20-ft PDU was used to establish a performance map for the vent streams expected from the recovery system of a slurry phase polyethylene process. The columns were filled with an adsorbent selected for ethylene. Over thirty experiments were completed to quantify nitrogen recovery and system productivity at different process conditions. The feed pressure for the experiments ranged from 180 to 350 psig, and the purge pressure ranged from 8 to 38 psig. The methane concentration in the feed ranged from 0 to 1%; the ethane concentration ranged from 0.4 to 4%; the isobutane concentration ranged from 0 to 14%; the ethylene concentration ranged from 3 to 30%; and the nitrogen concentration ranged from 54 to 94%. The purity of the nitrogen ranged from 99 to 99.9%. The differences in performance of the 4-column, 1- and 2-equalization cycles were quantified for several feed conditions.

Over this rather large range of feed and cycle conditions, the feed and recovery response to product purity shows the same general trends between 200- and 2000-ppmw C2+ hydrocarbon level (Figure 14).

Figure 14. Relative Feed Loading and Recovery Response to C2+ Impurity Level

At fixed cycle, feed composition and product purity, the overall performance was affected more by the ethylene feed concentration than by the isobutene feed concentration (Figure 15).

Figure 15. Relative Feed Loading and Recovery Response to Ethylene and Isobutane Feed Concentration

Increasing the purge pressure by 11 psi required a 20% decrease in the feed to maintain the same product purity. The nitrogen recovery decreased by 9% with the decrease in feed (Figure 16).

Figure 16. Relative Feed Loading and Recovery Response to Variations in Purge Pressure

Adding a step of pressure equalization following the purge step increased recovery by 2 to 3% at the expense of 10% in feed, depending on the amount of purge used (Figure 17).

Figure 17. Relative Feed Loading and Recovery Response to Relative Amount of Purge

A few experiments were done to optimize the adsorbent selection based on feed concentration of product purity specification.

For lighter components such as methane and ethane, the preferred material would have a higher surface area than that chosen for the initial screening experiments. The top five feet of the starting adsorbent were replaced with a high-surface-area material for methane adsorption. The data collected from eight experiments under various conditions suggest that a methane-selective adsorbent is required when the methane spec of the nitrogen product is less than 80% of the feed concentration. At the same level of ethylene in the nitrogen product, the addition of the high-surface-area material allowed for increased feed, due to a greater capacity for ethylene on the high-surface-area material; however, the nitrogen recovery decreased due to greater capacity for nitrogen as well, resulting in a greater loss to blowdown of adsorbed nitrogen. With the high-surface-area material on top of the columns, noticeably more time was required for the ethylene in the product to reach its steady-state level.

Choosing a smaller particle size analog (nominal particle diameter 2.1 mm) of the starting adsorbent (nominal particle diameter 2.4 mm) increased the feed rate by 8% and the recovery by four points.

The top four feet of the starting adsorbent were replaced with a low-surface-area adsorbent to decrease the amount of adsorbed nitrogen trapped in the top of the column at the beginning of blowdown. The feed rate increased by 2%, and the recovery increased four points.

When the columns were filled with 20 feet of low-surface-area material, the feed decreased by 20%, but the recovery stayed the same. The lower feed was the result of the lower ethylene

capacity of the low-surface-area material. The same recovery was the result of the lower nitrogen capacity of the material, resulting in lower blowdown loss of adsorbent nitrogen.

Gas Phase Polyethylene Process

Fourteen experiments were completed to quantify the PSA performance expected for nitrogen purification to 99.9 and 99.99% purity from streams expected in gas phase polyethylene applications. With a starting feed containing 26% ethylene and the constraint of equal volumes of blowdown and purge gas, raising the pressure from 180 to 250 to 340 to 500 psig allowed the feed to increase by 35%, 73%, and 124%, respectively to maintain 99.95% nitrogen purity. Over this range, the nitrogen recovery varied by less than 2 points; with a maximum occurring between 250 and 340 psig feed.

The addition of 5% 1-butene to the feed required a 3% decrease in the feed to maintain nitrogen purity, resulting in less than 0.5 point loss in recovery. Removal of the 1-butene, and the addition of 1% hexanes to the feed required a 5% decrease in the feed to maintain nitrogen purity, resulting in less than 0.5-point loss in recovery.

Gas Phase Polypropylene Process

Seven experiments were completed to quantify the PSA performance expected for nitrogen purification to 99.9 and 99.99% purity from streams containing 13 and 36% propylene. Increasing the propylene in the feed from 13 to 36% required a 10% decrease in feed, resulting in a one-point drop in recovery. The effect of adding 5% ethylene and propane on the PSA performance was also quantified: no change in PSA capacity occurred, and a slight increase in nitrogen recovery produced a nitrogen stream of 100 ppm propylene; however, 400 and 1000 ppm breakthrough levels of propane and ethylene decreased the overall purity. The system was modified to allow the introduction of 200 ppm n-hexene to the 35% propylene/nitrogen feed. The presence of hexene in the feed had no effect on the overall performance of the PSA after 4½ days of operation. Monitoring the gas phase along the column showed that the hexene was at the 12-ft level after 4½ days of operation, but not at the 14ft level.

Replacing the top four feet of adsorbent with a low-surface-area material to decrease the amount of nitrogen adsorbed on the column before the blowdown step increased the recovery by four points at similar feed and purity. Replacing the entire column with a low-surface-area material also increased the nitrogen recovery by about four points, but at a slightly lower feed rate.

Phase II: Recovery of Hydrogen from Refinery Off-Gas

Adsorption/Desorption of Hydrocarbons

Methane and Ethane

The effect of methane and ethane in the feed and was quantified with 10 feet of the high-surface-area adsorbent. The effect of product purity on overall performance was also determined by

increasing the feed rate to the columns. The cycle was 4/1/2, the feed pressure was 300 psig and the purge pressure was 7.5 psig. The on-feed time per bed was 180 seconds.

Increasing the methane level in the feed from 5 to 20% required a 14% decrease in the feed rate to maintain purity. The decrease cost about 1.5% in hydrogen recovery. Adding 10% ethane to the feed required another 14% decrease in the feed at the expense of 1.5% more in hydrogen recovery (Figure 18).

Figure 18. Relative Feed Loading and Hydrogen Recovery Response to Methane Breakthrough

Propane

The effect of adding propane to the high-surface-area adsorbent was quantified using the same cycle. The effect was quantified with either 5% methane or 10% ethane/20% methane balance hydrogen as the base case feed compositions. With ten feet of high-surface-area adsorbent, the feed required to maintain 99.99% hydrogen purity decreased linearly with increasing propane in the feed. The feed requirement response to propane level was the same for both starting cases. The recovery decrease associated with the increase in propane level was about half that for the case with 5% methane compared to the case with 10% ethane/20% methane in the feed (Figure 19).

Figure 19. Relative Feed Loading and Hydrogen Recovery Response to Propane Concentration in the Feed Gas

The need to add low- and/or medium-surface-area adsorbents as a protective layer was also determined. With no propane in the feed, the addition of one foot of the medium-surface-area adsorbent at the bottom of the bed decreased the performance: 5% in feed and 2% decrease in recovery. Addition of another foot of medium-surface-area adsorbent caused a similar decrease in performance. The benefit of the medium-surface-area adsorbent became evident as the level of the propane in the feed increased (Figure 20).

Figure 20. The Effect of Adding a Medium-Surface-Area Adsorbent to the Bed

For propane adsorption, the use of the medium-surface-area adsorbent provided better overall performance as a protective layer. Replacement of two feet of medium-surface-area adsorbent with two feet of low-surface-area adsorbent caused a 20% decrease in feed and a 4% decrease in hydrogen recovery (Figure 21).

Figure 21. The Effect of Adding Low- and Medium-Surface-Area Adsorbents to the Bed

Butane

Using the same cycle, the effect of adding n-butane to the high- and medium-surface-area adsorbent was quantified with 10% ethane / 20% methane as the base case feed composition. With ten feet of high-surface-area adsorbent, the feed required to maintain 99.99% hydrogen purity decreased significantly with a small amount of added n-butane, then decreased linearly with increasing levels. The feed requirement response to propane level was the same for both starting cases. With no n-butane in the feed, the addition of one foot of the medium-surface-area adsorbent at the bottom of the bed decreased the performance: 6% in feed and 2% in recovery. Addition of another foot of medium-surface-area adsorbent caused a similar decrease in performance. The benefit of the medium-surface-area adsorbent became evident at the lowest level of the n-butane in the feed (Figure 22).

Figure 22. The Effect of Adding a Medium-Surface-Area Adsorbent to the Bed with n-Butane in the Feed Gas

As with propane, the use of the medium-surface-area adsorbent provided better overall performance as a protective layer for n-butane. Replacement of two feet of medium-surface-area adsorbent with two feet of low-surface-area adsorbent caused an average 12% decrease in feed and a 2% decrease in hydrogen recovery (Figure 23).

Figure 23. The Effect of Adding Low- and Medium-Surface-Area Adsorbents to the Bed with n-Butane in the Feed Gas

Pentane

The adsorption of pentane on the medium-surface-area adsorbent was studied with a column loading of one foot of medium-surface-area adsorbent and nine feet of high-surface-area adsorbent. With 10% ethane, 20% methane, and 70% hydrogen as the starting point, n-pentane was added to the feed (replacing hydrogen) under the conditions given above. The pentane in the feed was stepped up in increasing levels for 8, 11, 9 and 6 days. It was difficult to determine if any of these experiments reached cyclic steady state. The methane level in the product continued to rise slowly. When the pentane level in the feed was decreased to half the maximum level, the methane in the product appeared to reach a constant level after 11 days. To maintain 100-ppm methane in the hydrogen product, the feed was lowered 8% compared to when there was no pentane in the feed. With this feed decrease, hydrogen recovery dropped 2 points. The level of pentane reaching the high-surface-area layer was between 100 and 200 ppm. Ten to 50 ppm of pentane was detected as far down as 4 feet into the high-surface-area layer. Samples were not taken farther down the bed. Removing the pentane from the feed for seven days did not return the performance to the starting point. To obtain 100 ppm methane in the product, the feed set point was still 7% lower than at the start. Pentane was still detected 4 feet into the carbon layer after seven days. The results show that the pentane is strongly held on the high-surface-area adsorbent, reducing its capacity for ethane and methane and decreasing overall performance (Figure 24).

Figure 24. The Effect of Adding Pentane to the Feed Gas with Medium-Surface-Area Adsorbent in the Bed

With the addition of another foot of medium-surface-area adsorbent, n-pentane was effectively held in the pretreatment layer at all levels in the feed with 10% ethane / 20% methane / balance hydrogen. The feed and recovery remained constant with pentane level from zero to the maximum level. When the two feet of medium-surface-area adsorbent was replaced with two feet of low-surface-area adsorbent, the feed decreased 10% and the recovery dropped 3%. This result was due to the lower adsorption capacity of ethane and methane on the low-surface-area material. At the same feed rate, the penetration of n-pentane into the pretreatment layer was slightly less with the low-surface-area adsorbent, indicating that this is the preferred material for pentane adsorption/desorption. The addition of 20% propane to the feed displaced enough of the pentane onto the high-surface-area adsorbent to cause a slow buildup, preventing a steady state with respect to hydrogen purity.

Hexane

The adsorption of hexane on the medium-surface-area adsorbent was studied with a column loading of two feet of medium-surface-area adsorbent and eight feet of high-surface-area adsorbent. With 10% ethane, 20% methane, and 70% hydrogen as the starting point, a mixture of hexanes was added to the feed (replacing hydrogen) under the conditions given above. Upon introduction of the hexane hydrocarbons, several weeks were required to establish steady-state adsorption-desorption on the medium-surface-area adsorbent. The concentrations of hexane and pentane were monitored one foot into the medium-surface-area adsorbent upon removal of n-pentane from the feed and introduction of hexanes. Once established, the concentrations came to cyclic steady state much faster following perturbations in feed or cycle conditions. N-pentane reached steady-state adsorption-desorption on the medium-surface-area adsorbent in 24 to 36 hours, but hexanes required 3 to 4 days. The addition of 20% propane to the feed displaced enough of the hexanes onto the high-surface-area adsorbent to cause a slow buildup, preventing a steady state with respect to hydrogen purity (Figure 25).

Figure 25. The Effect of Adding Hexane to the Feed Gas with Medium-Surface-Area Adsorbent in the Bed

At the same level of hexane in the feed and the same feed flow rate, the penetration of hexane into the low-surface-area adsorbent was slightly lower than that observed with the medium-surface-area adsorbent, indicating that low-surface-area adsorbent is the preferred material for hexane adsorption/desorption. At the same feed flow rate, the level of methane in the product was higher with the low-surface-area adsorbent. This result was due to the lower adsorption capacity of ethane and methane on the low-surface-area material. As with the medium-surface-area adsorbent, the addition of 20% propane to the feed displaced enough of the hexanes onto the high-surface-area adsorbent to cause a slow buildup, preventing steady state with respect to hydrogen purity. The level of methane in the product was significantly greater than when the medium surface area was used, demonstrating that the medium-surface-area adsorbent is preferred for propane. The addition of 0.1% water to the feed had no effect on the degree of hexane penetration into the low-surface-area adsorbent.

Toluene

With two feet of low-surface-area adsorbent and eight feet of high-surface-area adsorbent, toluene was added to the feed with 10% ethane, 20% methane and the balance of hydrogen. After eight days, toluene was detected two inches into the low-surface-area adsorbent, but not detected at six inches.

Feed with Mixed Heavy Hydrocarbons

With one foot of low-surface-area adsorbent, two feet of medium-surface-area adsorbent and seven feet of high-surface-area adsorbent, a series of experiments were completed to determine the amount of pretreatment adsorbent required under a wide range of conditions. The feed to the PSA contained toluene, hexane, pentane, butane, propane or carbon dioxide, ethane, methane, nitrogen and hydrogen. The feed pressure ranged from 250 to 450 psig, and the number of pressure equalizations ranged from one to three. The methane in the feed ranged from 6 to 25%, the ethane in the feed ranged from 4 to 15%, the propane in the feed ranged from 0 to 6%, and the carbon dioxide in the feed ranged from 0 to 15%. Axial sampling monitored the degree of penetration of the higher hydrocarbons into the pretreatment layer. After eight days, toluene was detected two inches into the low-surface-area adsorbent, but none was ever detected at six inches after four months of continuous operation.

The required pretreatment adsorbent layer increased with increasing levels of methane, ethane, propane, butane, and carbon dioxide in the feed. The required pretreatment adsorbent layer also increased with increasing purge pressure, but decreased with increasing feed pressure. This result was due in part to the fact that the level of C₄+ hydrocarbons in the feed had to decrease due to vapor pressure limitations. Changing the cycle to include more steps of pressure equalization had very little effect on the required level of pretreatment.

The hydrogen recovery and feed rate decreased with increasing levels of methane, ethane, propane, butane, and carbon dioxide in the feed. The hydrogen recovery and feed rate also

decreased with increasing purge pressure but increased with increasing feed pressure. Changing the cycle to include more steps of pressure equalization increased hydrogen recovery at the expense of lower feed rate.

Effect of Cycle Time on PSA Performance

The effect of cycle time on the overall performance of the PSA was studied using two different bed loadings: (1) ten feet of high-surface-area adsorbent and (2) six inches of low-surface-area adsorbent, 18 inches of medium-surface-area adsorbent and eight feet of high-surface-area adsorbent. The effect was quantified with and without the heavier (C_4+) hydrocarbons. The cycle had one step of pressure equalization. The adsorption was done at 250 psig, and the purge was done at 7 psig. For all systems studied (two different adsorbent loadings, with and without heavier hydrocarbons), decreasing the feed time caused the same decrease in the overall performance. Though the feed per cycle decreased with decreasing cycle time, the overall feed rate increased. The decrease in the feed per cycle required to maintain 100 ppm methane in the product and the resulting decrease in recovery was due to the higher feed rate, allowing the adsorbates less time to reach equilibrium with the adsorbents. Cutting the cycle time by two-thirds decreased the feed per cycle by 18% and the hydrogen recovery by 6%. The faster cycle meant that the rate of purified hydrogen increased by 130%, but at the expense of lower recovery. Measurements of the degree of penetration of heavy hydrocarbons into the protective adsorbent layers showed that these material adsorbates responded in the same way methane did on the high-surface-area adsorbent (Figure 26).

Figure 26. The Effect Reducing Cycle Time on Various Bed Configurations

Selection of Protective Layer Adsorbent

Other adsorbents were tested as pretreatment layer materials, using a cycle with one step of pressure equalization. The adsorption was done at 250 psig, and the purge was done at 7 psig. In one bed loading, the standard low-surface-area (1.8 mm nominal particle diameter) and medium-surface-area (2.3 mm diameter) adsorbents were replaced with small particle analogs with 0.9 mm and 1.0 mm nominal particle diameters, respectively. The small particles provide a

shorter diffusion length for the heavy adsorbates to enter and exit the adsorbent, but also provide greater pressure drop on the purge step, decreasing its effectiveness. For the conditions used in these experiments, these two competing effects resulted in no significant difference in the degree of penetration of the heavy hydrocarbons into the protective layer.

The low- and medium-surface-area adsorbents were replaced with an intermediate-surface-area material. If effective, the intermediate material alone would provide a means of simplifying column-loading procedures in the field. Under the conditions studied here, the intermediate-surface-area adsorbent had a performance inferior to the two-layer protection system.

Task 3: Demonstration in Commercial Operation

Phase I: Monomer Recovery

Air Products successfully demonstrated the high-performance PSA technology as part of a commercial Isobutane/Nitrogen Recovery Unit (INRU) supplied to Chevron Phillips Chemical Company (CPCChem) in January 2002. The system began commercial operation in June 2003. The elapsed time between the equipment supply and the system start-up was due to the construction schedule of CPCChem's overall project. The INRU is part of a new world-scale grassroots polyethylene unit located in Baytown, Tex. Figure 18 presents an overview of the process.

Figure 27

In the INRU process, the purge gas from the polyethylene plant containing N_2 , co-monomer, ethylene, and process diluent is compressed and then partially condensed. The hydrocarbons are recovered as liquids and pumped back to the polyethylene plant for re-use. The impure N_2 vapor produced by the partial condensation section is fed to the high-performance PSA. The PSA

removes the remaining hydrocarbons from the nitrogen, thereby producing a high-purity nitrogen product that is recycled back to the purge column of the polyethylene plant for re-use. The hydrocarbons removed by the PSA are contained in a low-pressure tail gas that is recycled back to mix with the incoming feed and is re-processed. The PSA technology allows nearly complete recovery of the N₂ molecules in the purge column gas. The INRU system takes in the purge gas stream and produces only reusable products. None of the incoming feed goes to waste. As a result of this highly efficient system, the INRU conserves the considerable energy and hydrocarbon feedstock resources used to produce the hydrocarbons and the nitrogen it recovers. Additionally, the PSA technology allows the INRU to recover materials that, under other circumstances, would have to be disposed of by burning. Avoiding the flaring of these hydrocarbons, the PSA technology also helps reduce NO_x, VOC, CO and CO₂ emissions associated with all or part of the purge gas.

The skidded equipment for a typical installation costs between \$2.5MM and 4.0MM. Customers experience simple payback periods that usually range from 18 to 24 months, based on the value of the recovered product. Any economic value assigned to the reduction of emissions would shorten the payback period.

The PSA N₂ product met purity requirements immediately upon start-up. The PSA and the overall system performed very well despite initial feed stream conditions that differed significantly from the design basis for the unit. Despite these differences, the PSA proved it could produce N₂ product at rates up to 150% of its design capacity.

In one incident, human error caused a problem with the operation of the PSA cycle, requiring reloading the beds with fresh adsorbent in November 2003. Changes to the control software were put in place to prevent this problem from recurring. Since the unit restarted, it has operated flawlessly.

The performance test for the PSA occurred on the week of 12 January 2004. During the test, we took the opportunity to further optimize the operation of the PSA. Figure 19 illustrates the results of the optimization work.

Figure 28

Results of PSA Optimization

During the optimization exercise, the PSA N₂ recovery improved over 50%. Increasing the PSA recovery dramatically improved the efficiency of the system. The feed flow to the PSA dropped by 56%. Lowering the gas flow through the entire system further reduced the INRU power consumption by about 10%.

Aside from proving the system can operate in a commercial polyolefin plant, the second goal of the demonstration was to prove the stability of the PSA technology over time. A second performance test held during the week of 1 April 2003 proved the PSA performance was stable over the interval from January through March 2003. Table 7 compares the N₂ recovery and bed loading measured during the two performance tests.

Table 7 – Comparison of N₂ Recovery and Bed Loading

	January 2004	April 2004
N ₂ Recovery	73%	78%
Bed Loading (mlbmol/lb adsorbent)	0.8	0.8

Table 7 shows that the PSA performance was very stable over the period. The hydrocarbon capacity of the adsorbent was unchanged. In addition, the N₂ recovery increased slightly in the later performance test. Our analysis of the data indicates that a slightly more favorable feed condition existed during the second test, which accounts for the slight increase in separation efficiency. The increase in N₂ recovery is not regarded as significant.

Customer feedback on the unit is very positive. The PSA, and indeed, the entire system, have performed with minimal operator attention since November 2003 and have never failed to meet

the design requirements for production capacity or product purity. In conclusion, Phase I, Task 3 has shown that the high-performance PSA technology can operate reliably and consistently in a commercial polyolefin production environment. Moreover, the technology is flexible, predictable, and continues to be commercialized.

Phase II: Refinery Off-Gas (ROG) H₂ Recovery

Because of commercial considerations, the demonstration of the ROG H₂ recovery PSA technology was cancelled. A more detailed discussion of the commercial aspects of this decision is provided below in Task 4: Commercialization.

The scope of the demonstration also proved problematic. A full-scale commercial demonstration was considered too risky by any of the refiners we approached. Conversely, we were told that a smaller scale demonstration that reduced the risk of mal-performance to the refinery operation did not provide sufficient value to refiners to justify their involvement. Despite considerable effort, we found no refiner willing to sponsor the demonstration.

Task 4: Commercialization

Phase I: Monomer Recovery

Our overall commercialization strategy is "controlled introduction" of the new technology. That is, the first stage of the strategy is to partner with an important and reputable end user, as we have done in this case with Chevron Phillips Chemical Co. (CPChem). This partnering effort provides a channel for acquiring information and valuable operating data specifically applicable to the customer's requirements for the final product. We successfully demonstrated the technology at the partner's operating facility. Air Products is prepared to expand the use of the technology to other CPChem sites and/or to other companies worldwide. For the case of monomer recovery systems, we are well positioned to become part of Phillips' standard offering for polyolefin plant process licensing packages.

In addition, since the successful sale of the commercial system to CPChem, in October 2002 Air Products sold a second monomer recovery system to another polyolefin manufacturer in the U.S. This second commercial unit successfully began operation in February 2004. This system, whose application is polypropylene production, operates in an existing facility and takes purge gas from multiple polypropylene production trains. These two applications nicely bracket the major market segments: from polyethylene production, to polypropylene production, to new grassroots, single, world-scale production units, to retrofitting existing polyolefin facilities with multiple small production trains.

These two units combined are recovering 14 MMlb/yr of monomer material and 33 MMlb/yr of nitrogen.

Energy Savings

Basis: 1 MMlb/yr of monomer recovered

Energy Source	Current Technology (Energy Used Per Year)	Proposed Technology (Energy Used Per Year)
Electricity (kWh)		-228,000
Natural Gas (cubic feet)		-470 MMSCF

Assumptions:

1. Since this technology recovers monomer and nitrogen that normally goes to flare, the energy savings are expressed as the energy saved by operating this process relative to the energy expended in generating the polymer-grade monomer and nitrogen products from scratch.
2. Specific fuel energy to produce the monomer (including steam export credit) = 2664 Kcal/Kg.
3. Specific electrical energy to produce monomer = 330 Kcal/Kg.
4. Steam credit taken against fuel consumption.
5. Fuel taken as natural gas.
6. Specific power to manufacture nitrogen = 0.85 kW/100 SCF.

Emissions Savings

Basis: 1 MMlb/yr of monomer recovered

Waste Generated	Current Technology (Tons/Year)	Proposed Technology (Tons/Year)
CO ₂		-34.8 MM Tons of Carbon Equiv.
Greenhouse Gases		-4.8
Carbon Monoxide		-47.6
SO ₂		-109
NO _x		-280
VOCs		-2.6

Assumptions:

1. Since this technology recovers monomer and nitrogen that normally goes to flare, the emissions reductions are expressed as the emissions avoided by operating this process relative to the emissions that come from generating the energy expended in producing the polymer-grade monomer and nitrogen products from scratch.
2. See Assumptions 2-6 in above.

Phase II: Refinery Off-Gas (ROG) H₂ PSA

Our intent in ROG H₂ PSA was to follow the same successful strategy used for the monomer recovery application. However, several factors conspired to limit our ability to commercialize this technology. As we learned more about the market for H₂ PSA systems, we found that the incumbent leader in the market was willing to substantially reduce its price to retain a leadership position. In the end it appeared that Air Products could not garner the volume of business

needed to support a cost structure that is competitive in this market segment. As result, the management of the company recently decided to exit the business of selling H₂ PSA units as equipment. However, we retained the capability to design and produce a H₂ PSA that might handle ROG as part of our sale-of-gas business.

The refiners' market situation was also problematic. The refiners are currently working through a transition to low-sulfur clean fuels. A large amount of additional hydrogen is required by refiners to meet their needs for producing low-sulfur fuels, often 40 to 100 MMSCFD. Because these new needs are so large, most refiners are adding new "on-purpose" hydrogen production units. The amount of hydrogen recovered by most PSA applications will be far less than required. Therefore the refiners are forgoing investment in the incremental hydrogen capacity that could come from PSA recovery projects and focusing on building the large "on-purpose" hydrogen production systems. Our market feedback is that it may be 5 or more years before the incremental hydrogen that could be recovered by PSA technology from difficult refinery off-gases will become attractive. This feedback provides the second reason for our decision to exit this market.

The ultimate result of all these market forces is that we decided not to pursue the demonstration task and commercialization of the ROG H₂ PSA technology. We will utilize the research to improve the monomer recovery PSA offering and H₂ PSA technology where the opportunity arises as part of a sale of hydrogen gas.