BASF Catalysts LLC (formerly Engelhard Corporation)

Cost-Efficient Process for Increasing Natural Gas Production

In the late 1990s, natural gas supplied about 23 percent of the total energy used in the United States. Behind only oil, natural gas was the second-largest source of energy for industry, consumers, and commercial use. However, as much as 16 percent of all untapped natural gas in the United States is contaminated with excessive levels of nitrogen (N_2), and such fields are often overlooked because these resources are too costly to purify. In addition to nitrogen, the main constituent in natural gas, methane (CH_4), is also contaminated by various other gases. State-of-the-art purification processes involved multiple steps and were expensive. But in 1999, Engelhard Corporation proposed using its new Molecular Gate[1] adsorbent based technology, which separated nitrogen from methane, to make small and medium-sized fields and other sources of natural gas available through the cost-effective, single-step removal of all contaminants. Engelhard also envisioned applying Molecular Gate adsorbent based technology to other molecular separation applications, including oxygen (O_2) enrichment (separating oxygen from nitrogen). The technology would provide higher quality yet less expensive oxygen to the healthcare industry for patients who needed enriched oxygen or for the many other uses for enriched O_2.

Needing both financial and research assistance, Engelhard turned to the Advanced Technology Program (ATP) in 1999 and received an award for a three-year project. With ATP funding, Engelhard formed three industry-academia research collaborations to advance natural gas purification and to develop other molecular separation processes. At the conclusion of the project in late 2002, Engelhard had successfully created a single-step process to purify natural gas. Its technical achievements led to nine patents as well as the publication of numerous journal and news articles. Engelhard's Molecular Gate technology also won the 2005 Kirkpatrick Chemical Engineering Achievement award.

As of May 2006, Engelhard's ATP-supported advanced Molecular Gate adsorbent based technology was being marketed as its Carbon Dioxide (CO_2) Removal, and Nitrogen (N_2) Rejection systems. These systems operate at 18 small and medium-sized natural gas facilities. As a direct result of the ATP-funded project, Engelhard is able to help numerous small energy companies bring previously untapped natural gas resources online and into homes across America. In June 2006, BASF Aktiengesellschaft acquired Engelhard Corporation for an estimated $5.6 billion, and in August 2006 renamed the company BASF Catalysts LLC.

COMPOSITE PERFORMANCE SCORE
(based on a four star rating)
* * * *

Research and data for Status Report 99-01-6041 were collected during May – June 2006.

Production of Natural Gas Faces Challenges

The clean-burning natural gas used in American homes and by industry is pretreated prior to pipeline transmission to almost pure methane (CH_4). But as it comes out of the ground, and at the wellhead, natural gas is considered "wet," because it contains numerous impurities. Although still composed of 70- to 90-percent

[1]Molecular Gate is a registered trademark of BASF Catalysts LLC

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methane at this stage, other constituents, including nitrogen (N_2), carbon dioxide (CO_2), hydrogen sulfide (H_2S), and water (H_2O), are present at levels that can vary widely in the overall composition of this product. In order for natural gas to go through the large system of U.S. pipelines for transportation and processing, high concentrations of inert gases and non-hydrocarbon compounds must be significantly reduced. High levels of inerts (nitrogen and carbon dioxide) and potentially corrosive non-hydrocarbons (water, hydrogen sulfide, and carbon dioxide) in natural gas can cause operational challenges and pipeline deterioration. Nitrogen, for example, can be present in wellhead natural gas at levels as high as 30 percent or more; however, this gas cannot enter the pipeline system at higher than 4 percent of the total composition, as deemed by the U.S. Interstate Transmissions Standards.

Due to the high cost and complexity of lowering the level of nitrogen and all other impurities at the wellhead, many small and medium-sized production facilities left known natural gas reserves in the ground.

In the late 1990s, the cost of lowering the level of nitrogen and all other impurities at the wellhead was high and involved three different processes: amine for carbon dioxide and hydrogen sulfide processing, glycol or molecule sieve dehydration for water, and extremely low temperature cryogenic processing for nitrogen. Due to the high cost and complexity of building and operating these systems, many small and medium-sized production facilities left known natural gas reserves in the ground. In the late 1990s, as much as 16 percent of all natural gas in the United States was contaminated with nitrogen and often untapped because of the high cost of removing contaminates at the wellhead.

Engelhard Discovers Breakthrough Separation Process

In the late 1980s and early 1990s, Engelhard Corporation achieved a laboratory breakthrough in gas molecule separation that was based on molecule size. By applying precise temperature change to the atomic framework of a molecular sieve, Engelhard was able to create a molecular sieve by shrinking pore sizes through a process of dehydration (as depicted in Figure 1). (Molecular sieves are “zeolytes” that are crystalline structures with precise cavity sizes such that small molecules can enter the pores and be selectivity removed while larger molecules are excluded, hence the term “sieve.”) Engelhard’s newly designed molecular sieve compositions then “trapped” certain sized contaminates that passed into the pores. Unlike existing molecular separation systems, Engelhard’s technology is able to trap targeted, contaminated natural gas molecules as they come out of the ground at high pressure, at the wellhead, and then release these molecules at low pressure, all while the higher value methane molecules continue through the process at high pressure. This process of adsorption decreases the level of the less desirable molecules in natural gas. Relying on this effective and efficient material called Molecular Gate adsorbent, Engelhard’s objective was to tap the otherwise expensive-to-process, underground natural gas reserves and bring purified, more usable gas into homes across America. Engelhard also saw the possibility of expanding its Molecular Gate adsorbent technology to generate low-cost oxygen-enriched air, which was used in a wide range of applications.

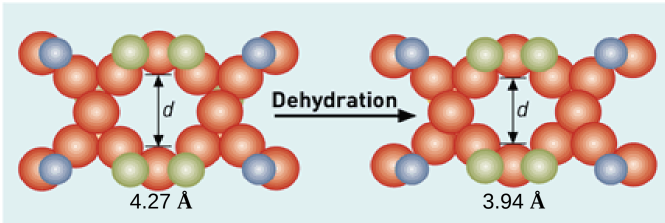

Figure 1. The result of high-precision dehydration on a framework of atoms. Depicted on the left is a group of various atoms at room temperature. The diameter (*d*) of the opening is 4.27 Angstrom (Å). After the precise application of heat to the atoms in this framework, up to 250°C, dehydration occurs, shrinking the structure and reducing the molecular opening to a diameter of 3.94 Å, as depicted on the right. The change represents a controlled, eight-percent shrinkage of the molecular opening required for precise separations. The smaller opening does not permit larger, desirable gas molecules from entering the framework opening. The smaller, undesirable molecules, however, can enter the framework and become trapped within the sieve.

Based on Engelhard’s ability to precisely manipulate material pore size, the company considered the possible separation of molecules of almost identical size. In the case of methane and nitrogen molecules, for instance, methane molecules are 3.8 Å (an angstrom is 10^{-8} cm) while nitrogen molecules are 3.6 Å. Through dehydration, Engelhard was able to successfully tune sieve adsorbents so that they could trap the smaller, undesirable nitrogen molecules and allow the larger, desirable methane molecules to move through this natural gas process at feed or wellhead pressure. Thus, nitrogen levels in this contaminated gas are reduced and the natural gas meets pipeline specifications. Molecular sieve adsorbents used at the time were set at fixed and not adjustable pore sizes (such as 4.0, 5.0, and 10.0 Å) and, therefore, were not effective. The company's ability to construct a molecular framework or gate with smaller, precisely controlled pore sizes using calcination (the process of heating a substance to a high but controllable temperature) advanced the science of molecular separation to involve multiple containment separations. Engelhard envisioned, for the first time, the simultaneous removal of nitrogen, water, carbon dioxide, and hydrogen sulfide from natural gas. Indeed, Molecular Gate adsorbents would allow for the one-step purification of natural gas.

Engelhard also foresaw the possibility of using its process to separate molecules of even closer size, such as in the process used to enrich oxygen to produce transportable medical oxygen for use in portable hospital and home patient oxygen systems. Applying Molecular Gate adsorbents to other gas separations would require a high level of precise, reproducible, and robust controls of the pore sizes, because different molecules or compounds in an air mixture are attracted and held by a molecular sieve adsorbent surface at different levels effectiveness. Furthermore, temperature applications to gate pores that might work for nitrogen/methane separation would not necessarily work for oxygen/nitrogen separation.

Engelhard also intended to improve existing Molecular Gate materials for use in the zeolitic membranes to achieve higher levels of separation. (Zeolite membranes are unique crystalline structures bonded together to allow small molecules to pass through the membrane barrier while preventing larger molecules from doing so.) The development of new techniques for improving the quality and performance of zeolite membranes would involve temperature adjustment and cation exchange, a process by which membrane structures are adjusted by incorporating different-sized molecules within the molecular sieve framework to adjust the pore size. For example, replacing larger molecules with smaller molecules would make the gate opening larger and vice versa. But combining temperature adjustment with cation exchange would be a challenge. Engelhard decided they needed assistance and formed a team with VTI Corporation, Cleveland State University, and the University of Massachusetts as subcontractors. Engelhard then applied for ATP cost-shared funding in April 1999 and began work on their project in December 1999. With assistance from its subcontractors, Engelhard concurrently executed three project objectives from December 1999 to November 2002. These objectives were: 1) simplified natural gas purification, 2) oxygen enrichment of air streams, and 3) molecular technology advancement through dehydration and ion exchange.

Team Simplifies Natural Gas Purification

A primary goal of the ATP-funded project was to develop a single-step process to purify natural gas. Engelhard sought to reduce the levels of nitrogen, carbon dioxide, water, and hydrogen sulfide in methane by separating the larger methane molecules from the smaller non-hydrocarbon contaminate molecules using its Molecular Gate adsorbent. Current state-of-the-art purification processes consisted of expensive, multistep procedures such as acid gas removal, glycol or molecular sieve dehydration, and low temperature (cryogenic) distillation. Engelhard's proposed process at the wellhead would open up small and medium-sized natural gas fields and would reduce contaminates in natural gas to permissible levels for pipeline transportation and processing. Figure 2 depicts Engelhard's molecule separation objective.

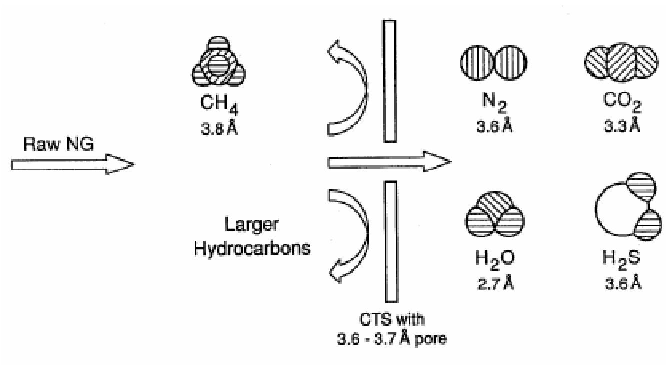

Figure 2. Single-step, multiple-contaminant purification of natural gas. As raw natural gas (NG) from the wellhead enters the purification process at a high pressure, numerous smaller, undesirable gas molecules, such as nitrogen (N_2), carbon dioxide (CO_2), water (H_2O), and hydrogen sulfide (H_2S), enter the contracted titanosilicate (CTS) framework opening and are trapped inside the sieve, while the larger methane molecules (CH_4) continue to flow through the natural gas process. Because the CTS is precisely tuned to the 3.6 Å to 3.7 Å pore size, the removal of multiple contaminants is possible in a single-step process.

Prior to beginning the ATP-funded project, Engelhard had already demonstrated, in a laboratory setting, its ability to separate methane and nitrogen molecules. The major challenge would be in adjusting molecular structures by applying a precise amount of heat and thereby producing an appropriate level of dehydration to shrink the pores. The deft application of heat to control shrinkage would allow for the separation of multiple contaminants. Existing technology had proven that the framework of the titanium silicate ETS-4, the first member of this type or class of materials, could be systematically contracted through dehydration at elevated temperatures to "tune" the desired size of the pores, thereby giving only small molecules access to the interior of the sieve. These adjusted structures would then be fabricated into a fixed-bed, molecular sieve processing system and delivered on-site for natural gas field purification.

Engelhard Achieves Success in Nitrogen/ Methane Separation

During the first year of the project, Engelhard and VTI Corporation performed extensive isothermal (constant temperature) work on existing adsorbent materials. This work demonstrated that high levels of carbon dioxide adsorption capacity could be achieved. At this stage, the ability to separate methane and carbon dioxide, in addition to methane/nitrogen separation, appeared possible. However, Engelhard's research indicated that during methane/carbon dioxide separation, there was a substantial loss of crystallinity of the zeolite framework as a pore constricts in response to dehydration, irrespective of the conditions used to reach the contraction. The loss of crystallinity was undesirable because it decreased the level of control or tuning possible on the molecular framework.

Engelhard's technology is able to trap targeted, contaminated natural gas molecules as they come out of the ground at high pressure.

Also, progress in the area of nitrogen/methane separation led to a semi-commercial, field demonstration of nitrogen removal. In August 2000, Engelhard began work at the Tom Brown Inc. Hamilton Creek, Colorado natural gas production facility. The Molecular Gate adsorbent based technology successfully lowered the level of nitrogen on-site from a range of 15 to 18 percent to a range of 3 to 5 percent.

In the second year of the ATP-funded project, Engelhard developed simplified natural gas processes to simultaneously remove carbon dioxide and nitrogen from methane. This achievement proved the concept of single-step purification involving multiple contaminate gases in processing natural gas. This was a breakthrough, because one-step carbon dioxide and nitrogen removal from methane represented the most significant opportunity for natural gas purification. Additionally, Molecular Gate nitrogen removal material demonstrated unique size-separation properties, and these materials were superior to commercial, state-of-the-art carbon dioxide adsorbents. While Molecular Gate materials proved more expensive than conventional adsorbents, the ability of Molecular Gate adsorbent to perform multiple gas contaminate removal, which conventional adsorbents cannot achieve, made it unique.

Through further advances, Molecular Gate materials could also separate water molecules from methane. At the conclusion of the second year of research, Engelhard had achieved both technical and application success: single-step nitrogen, carbon dioxide, and water removal and a viable market for advanced Molecular Gate adsorbent based technology. During year three development, however, Engelhard discovered that there was a limited market and therefore limited need for advancements in Molecular Gate materials in the area of hydrogen sulfide removal. Existing processes for hydrogen sulfide were well-established and effective. Therefore, the company focused its natural gas purification efforts exclusively on advancing breakthroughs involving the single-step removal of water, nitrogen, and carbon dioxide from methane. This process would eliminate the currently used difficult, multiple step, and expensive systems and would lower natural gas production costs in a simplified process.

Oxygen Enrichment of Air Streams

The air we breathe, ambient air, is made up of 21 percent oxygen (O_2). It also comprises 78 percent nitrogen and 1 percent of traces of eight other gases. Mildly enriched oxygen (at 30 percent oxygen) dramatically improves combustion in industrial uses. At 30 percent, mildly enriched oxygen is known to influence flame temperature and burning efficiency for diesel engines, blast furnaces, and heating systems. Highly pure oxygen (at 90 percent or greater) is used in the healthcare field, often as transportable oxygen to support patient breathing. But while oxygen is the third-largest bulk chemical produced in the United States (more than 650 trillion cubic feet/year produced in 2000), state-of-the-art oxygen generation for small, on-site facilities is expensive.

In 1999, smaller scale oxygen enrichment processes called for energy-intensive adsorption technology, typically involving the use of LiX zeolites. As a secondary project objective, Engelhard wanted to apply its Molecular Gate adsorbent based technology to the low-cost, simplified production of oxygen-enriched air. Engelhard would attempt to modify the properties of existing Molecular Gate adsorbents to separate oxygen from nitrogen molecules, focusing on pore size and the binding strength of adsorbents. The key to success would be in balancing adsorption rates (the flow of air) with oxygen selectivity (pore separation). Figure 3 depicts the type of separation Engelhard sought.

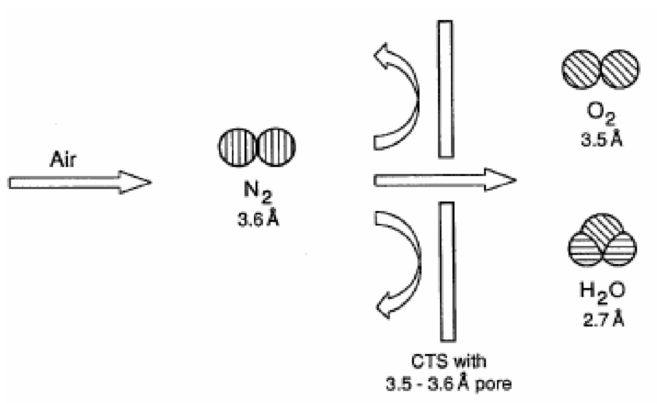

Figure 3. Oxygen enrichment of air. As ambient temperature air enters the purification process, smaller gas molecules, oxygen (O_2) and water (H_2O), enter the CTS framework opening and are trapped in the sieve. The larger, desired nitrogen (N_2) molecules are processed through the purification system.

Despite months of effort, Engelhard was unable to achieve a high level of oxygen/nitrogen separation. A highly porous structure hampered the separation of the oxygen and nitrogen molecules and led to low oxygen adsorption capacity. While the company attempted to solve this problem, it realized that both high oxygen capacity and high oxygen/nitrogen selectivity were hurdles they could not overcome for high-purity oxygen enrichment. Engelhard thought that the low capacity and selectivity problems were linked to crystallinity loss due to handling or "steaming," but later determined that crystallinity loss was actually a structural change inherent in the pore shrinkage. Engelhard changed its focus to a low enrichment nitrogen and oxygen separation system for industrial combustion applications.

By the end of year three, however, the company was unable to develop an adsorbent that was competitive with the molecular sieve, the existing process for producing oxygen for industrial use. Simply stated, Engelhard's adsorbent material, titanium silicate zeolites, suffered from limitations that they were not able to overcome, including low oxygen capacity. This part of the project ended with an eleventh-hour finding that crystallinity loss could be better avoided by using ion or cation size selection (the exchange of molecules) rather than framework shrinkage to control the pore size.

Advances Sought through Dehydration and Ion Exchange

While Engelhard was working on natural gas separation and oxygen enrichment, they also sought to expand current separation technology by altering existing Molecular Gate zeolitic membranes. This ATP-supported task represented the highest level of technical risk associated with the entire project.

The task was to advance Engelhard's first-generation separation membranes by using both dehydration and ion exchange. Engelhard envisioned using ion exchange to change the framework or chemistry of the molecular sieve so that the potential area imposed by the pore surface would be strong enough for selective adsorption, but weak enough to allow desirable transport or flow rates. Engelhard believed careful temperature changes to alter the dimensions of the membrane structure would allow better molecule selection, but they would be careful to avoid using so much heat that they would damage the membrane. This process would be coupled with ion exchange to expand the possibilities for Molecular Gate adsorbent based technology. The objective was to create macroscopic, defect-free zeolitic membranes with high flux (flow) and high selectivity (pore size separation) for air, natural gas, and other separations. The key to success in this task, as with oxygen enrichment, was balancing molecule selectivity with the ability to adsorb and hold certain molecules.

While Engelhard was able to advance specific technical areas of the overall objective, after two years of the three-year project, the researchers failed to reach their intended goal and the task was ended. University of Massachusetts researchers were successful in controlling crystal growth to a certain degree by combining ETS-4 and ETS-10 adsorbent materials, but they could not create membranes that came close to this task's goals. Changes in crystalline structure inherent in pore shrinkage caused membrane cracking that resulted in seriously low levels of flux and also reduced molecule selectivity. Researchers were not able to prevent cracks in the membrane nor could they raise fluxes to practical levels for real-world utility. Experiments in this area revealed that highly selective materials would fall short on flux, and of course, high-flux materials fell short on selectivity. Although there was some chance of success in controlling changes in crystallinity, the team members had agreed that for the final year of the ATP-funded project, staff resources would be more effectively used to apply the knowledge gained about control of crystalline morphology (form or shape) to improving levels of molecule selectivity in natural gas.

Technical Success Leads to Real-Life Application

The technical advancement of Engelhard's Molecular Gate adsorbents led to practical industrial application. In addition to the successful Hamilton Creek methane/nitrogen separation process demonstrated during the ATP-funded project (August 2000), Tidelands Oil began using the Molecular Gate adsorbent based system in 2004 to remove carbon dioxide and water from oil production-associated natural gas (the Tidelands facility is depicted in Figure 4). The Tidelands facility was the first commercial application of Engelhard's carbon dioxide and water removal system using Molecular Gate adsorbent. According to James Willis, Staff Engineer for Tidelands' Long Beach Operations, "The system allows us to generate a revenue stream from the sale of gas that otherwise would have to be flared [unusable gas that is burned off]. We selected the Molecular Gate adsorbent based system over commonly used amine technology due to its lower cost, simplicity of operation and environmental friendliness." While amine technology is capable of removing carbon dioxide from natural gas, it is unable to remove water. In this particular application, Molecular Gate adsorbents work by trapping carbon dioxide and water molecules in a fixed bed of adsorbent materials while allowing methane to pass through at feed pressure.

Figure 4. Tidelands Oil Facility. Engelhard's Molecular Gate molecular sieve is contained in a series of pressure vessels. The separation and purification process occurs within these pressure vessels.

Another impressive application of Engelhard's Molecular Gate adsorbent based technology has been at a southern Illinois operation. Since 2005, Grayson Hill Energy has been removing nitrogen, water, and carbon dioxide from gas produced from its coal mines and natural gas wells. In a single, unattended step, the Grayson facility system uses an integrated dehydration unit to remove water and simultaneously remove about 7 percent carbon dioxide and 12 percent nitrogen while delivering a product with less than 4 percent nitrogen. "We are pleased that this system enables us to bring gas to pipeline purity and allow the delivery to an interstate pipeline," says Steven Sisselman, President of Grayson Hill Energy. "The Molecular Gate adsorption [based] system helped give us a valuable new revenue stream." The Engelhard technology allows Grayson to treat up to 2.5 million standard cubic feet of natural gas per day. This system is located at the wellhead and is powered by an on-site gas-driven generator that uses as fuel the tail gas (waste methane) from the Molecular Gate adsorbent based processes.

During the ATP-funded project, Engelhard filed nine patents and published numerous trade journal articles and presentations. In 2005, the company won the prestigious Kirkpatrick Chemical Engineering Achievement Honor Award for its Molecular Gate adsorbent based technology. Also in 2006, Engelhard granted Guild Associates of Dublin, Ohio a license to manage the application of its Molecular Gate adsorbents. As of May 2006, this ATP-supported technology was marketed as Engelhard's Molecular Gate Adsorbent based System – Carbon Dioxide (CO_2) Removal, and Nitrogen (N_2) Rejection systems. Molecular Gate technology is being used at 20 different facilities across the United States. Guild Associates receives more than 100 requests for quotations for new Molecular Gate systems each year, and the technology is expected to be used in 6 to 12 new natural gas fields each year. Figure 5 shows the installation of a newly fabricated, custom designed, nitrogen-removal, Molecular Gate adsorbent containing natural gas processing unit.

Figure 5. The footprint of this small, nitrogen removal unit is 8 by 25 feet, with vessels, vacuum pump, instrument air system, valves, and instrumentation atop. (Compression unit and other peripheral items are not shown.) This skid weights about 25,000 pounds and is shipped on a double-drop truck. A crane is needed for installation.

In June 2006, BASF Corporation acquired Engelhard Corporation for an estimated $5.6 billion, and in August 2006 renamed the company BASF Catalysts LLC.

Conclusion

Hoping to achieve a breakthrough in molecule separation, in 1999 Engelhard Corporation sought to expand the use of molecular sieve adsorption in natural gas purification and to apply advances in this technology to other molecule separation possibilities, including oxygen/nitrogen purification. Engelhard wanted to apply its existing Molecular Gate adsorbents technology to the single-step purification of natural gas in order to reduce the levels of multiple natural gas containments. Such advances would replace costly, multiple-step natural gas processing. Engelhard also wanted to use this technology to more cost-efficiently enrich oxygen by separating nitrogen from the oxygen molecules. After enlisting the assistance of several subcontractors, in April 1999, Engelhard applied to ATP for financial assistance. From December 1999 to November 2002, Engelhard and its partners developed their innovative gas molecule separation technology.

At the conclusion of the project in 2002, Engelhard had successfully advanced molecular sieve adsorbent-based separation in the area of natural gas purification. The company's Molecular Gate adsorbents could separate several undesirable gas molecules from the higher value methane molecule in a simplified process. This innovation garnered Engelhard nine patents and led to the publishing of numerous journal and news articles in this area. In 2005, the Molecular Gate adsorbent based technology earned a Kirkpatrick Chemical Engineering Achievement award. After granting Guild Associates of Ohio permission to independently supply the technology in 2006, the technology is positioned to continue to assist energy companies in natural gas processing. Such processing included its Molecular Gate Adsorbent System: Carbon Dioxide (CO_2) Removal, and Nitrogen (N_2) Rejection units.

As of 2006, the technology was being used in 19 different facilities across the country, with more than 100 quotations for new systems requested each year. Molecular Gate adsorbents are expected to be in operation in 6 to 12 new facilities each year. Indeed, the introduction of a single-step, low-cost natural gas purification process allows small and medium-sized energy companies to bring to the surface and into American homes natural gas that was otherwise untapped. In June 2006, BASF Aktiengesellschaft acquired Engelhard Corporation for an estimated $5.6 billion, and in August 2006 renamed the company BASF Catalysts LLC.

PROJECT HIGHLIGHTS
BASF Catalysts LLC (formerly Engelhard Corporation)

Project Title: Cost-Efficient Process for Increasing Natural Gas Production (Application of Molecular Gate Technology to Oxygen Enrichment of Air Streams and Simplified Purification of Natural Gas)

Project: To build and demonstrate advanced separation technologies that will enable the one-step purification of natural gas and the generation of oxygen-enriched airstreams, thereby reducing the cost of natural gas purification, increasing marketable natural gas reserves, improving the economics of transportable oxygen for medical needs, and providing for cleaner-burning diesel engines.

Duration: 12/1/1999 - 11/30/2002
ATP Number: 99-01-6041

Funding (in thousands):

ATP Final Cost	$1,790	39.9%
Participant Final Cost	2,700	60.1%
Total	$4,490	

Accomplishments: With ATP funding, Engelhard Corporation developed a simplified, cost-effective process for the purification of natural gas. The company accomplished the following objectives:

- Single-step separation of carbon dioxide (CO_2) and water (H_2O) from methane (CH_4)
- Single-step separation of nitrogen (N_2), carbon dioxide, and water from methane (CH_4)

In 2005, Engelhard's Molecular Gate adsorbent based technology earned a Kirkpatrick Chemical Engineering Achievement award.

Engelhard Corporation received the following patents for technologies related to the ATP-funded project:

- "Polymorph-enriched ETS-4"
  (No. 6,464,957: filed August 15, 2000; granted October 15, 2002)
- "Water purification using titanium silicate membranes"
  (No. 6,340,433: filed September 15, 2000; January 22, 2002)
- "Geometric separation processes involving modified CTS membranes"
  (No. 6,395,067: filed September 15, 2000; granted May 28, 2002)
- "Simplified methods of manufacturing titanium silicate membranes"
  (No. 6,486,086: filed September 15, 2000; November 26, 2002)
- "Selective removal of nitrogen from natural gas by pressure swing adsorption"
  (No. 6,315,817: filed October 30, 2000; granted November 13, 2001)
- "Selective removal of nitrogen from natural gas by pressure swing adsorption"
  (No. 6,444,012: filed October 30, 2000; granted September 3, 2002)
- "Pressure swing adsorption process"
  (No. 6,497,750: filed February 26, 2001; granted December 24, 2002)
- "Olefin separations employing CTS molecular sieves"
  (No. 6,517,611: filed July 23, 2001; February 11, 2003)
- "Heavy hydrocarbon recovery from pressure swing adsorption unit tail gas"
  (No. 6,610,124: filed March 12, 2002; granted August 26, 2003)

Commercialization Status: The intellectual property and technology is now owned by BASF Catalysts LLC (formerly Engelhard Corporation). Guild Associates Inc. of Dublin, Ohio holds a USA and multi-national license for the design and supply of two types of Molecular Gate natural gas purification processing systems. These two systems are: Single-step separation of carbon dioxide and water from methane, and the single-step separation of nitrogen, carbon dioxide, and water from methane. In May 2006, 19 natural gas plants were using the Molecular Gate adsorbent based technology.

Outlook: The outlook for BASF Catalysts' Molecular Gate adsorbent based technology is strong. Simplified purification of natural gas is a growing need. U.S. gas reserves are limited, and price increases in natural gas have helped to justify the added cost for the removal of contaminates, such as nitrogen and carbon dioxide. Market interest has been consistently high, with more than 100 requests for quotations for Molecular Gate technology each year. Overall, the efficacy of the removal/rejection systems has been excellent and the timing for market conditions, including increased national

PROJECT HIGHLIGHTS
BASF Catalysts LLC (formerly Engelhard Corporation)

sentiment toward an emphasis on energy sources other than oil, has been very favorable.

Composite Performance Score: * * * *

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- Cleveland State University
  Advanced Manufacturing Center
  Cleveland, OH
- University of Massachusetts
  Chemical Engineering Department
  Amherst, MA
- VTI Corporation
  Hialeah, FL

Publications:

- Braunbarth, Carola, et al. "Structure of Strontium Ion-Exchange ETS-4 Microporous Molecular Sieves." *Chemistry Materials*, 2000.
- Braunbarth, Carola M., et al. "Synthesis of ETS-4/TiO2 Composite Membranes and Their Pervaporation Performance." *Journal of Membrane Science*, Vol. 174, Is. 1, pp. 31-42, July 2000.
- Nair, Sankar, et al. "Synthesis and Structure Determination of EST-4 Single Crystals." *Chemistry of Materials*, 2001.
- Nair, Sankar. "A Study of Heat-Treatment Induced Framework Contraction in Strontium-ETS-4 by Powder Neutron Diffraction and Vibrational Spectroscopy." *Journal of American Chemical Society*, 2001.
- Mitariten, Michael. "New Technology Improves Nitrogen-Removal Economics." *Oil and Gas Journal*, April 23, 2001.
- Kuznicki, Steven, et al. "A Titanosilicate Molecule Sieve with Adjustable Pores for Size-Selection Adsorption of Molecules." *NATURE*, Vol. 412, August 16, 2001.
- Wood, Andrew. "Engelhard's Adjustable Sieve." *Chemical Week*, August 22, 2001.
- Jeong, Hae-Kwon, et al. "Oriented Molecular Sieve Membranes by Heteroepitaxial Growth." *Journal of American Chemical Society*, 2002.
- Tsapatsis, Michael. "Molecular Sieves in the Nanotechnology Era." *American Institute of Chemical Engineers*, Vol. 48, Is. 4, pp. 654-660, April 2002.
- Jeong, Hae-Kwon. et al. "A Highly Crystalline Layered Silicate with Three-Dimensionally Microporous Layers." *Nature Materials*, pp. 53-58, 2003.
- Mitariten, Michael. "Economic Nitrogen Removal." *Hydrocarbon Engineering*, July 2004.

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