Demonstration of Carbon Capture and Sequestration of Steam Methane Reforming Process Gas Used for Large-Scale Hydrogen Production

FINAL REPORT

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ABSTRACT

The large-scale, on-purpose production of hydrogen in the United States (i.e., ~4600 million standard cubic feet per day) represents one of the most significant industrial sources of CO_2 emissions within the chemical industry. Most of the hydrogen is produced by the steam methane reforming (SMR) process, through which methane and water are converted to H_2 and CO_2, and virtually all of the co-produced CO_2 is emitted to the atmosphere. However, the process streams in the SMR plants contain CO_2 at concentrations that are amenable to utilization of conventional adsorption and emerging CO_2 capture technologies. If implemented commercially, these technologies could represent an early and sizeable impact in reducing industrial CO_2 emissions. Therefore, Air Products, working closely with the Department of Energy, has conducted a carbon capture and sequestration (CCS) project to demonstrate a first-of-a-kind retrofit system to capture CO_2 from large-scale industrial SMR plants.

Working with the support of Denbury Onshore, LLC ("Denbury Onshore") and its affiliate, Denbury Green Pipeline-Texas, LLC ("Denbury Green Pipeline"), Air Products designed, constructed and continues to operate a state-of-the-art system located at the Valero Port Arthur Refinery in Port Arthur, TX. This system concentrates the CO_2 from two SMR waste streams and delivers it into the Green Pipeline-Texas for transport to and use in the West Hastings Unit enhanced oil recovery (EOR) project. The CO_2 removal units were designed by Air Products and utilize vacuum swing adsorption (VSA) units that were retrofitted into each of the SMR trains upstream of existing pressure swing adsorption (PSA) units.

This project is unique because the site has two large-scale, highly integrated SMRs located in proximity to one another. The CO_2 from this project is concentrated from 15% in the SMR waste stream to at least 98%, then flowed into the Green Pipeline-Texas along the eastern Gulf Coast. The Green Pipeline collects CO_2 from a variety of sources that is utilized for tertiary oil recovery in Texas. This project alone can prevent over 1 million tons per year of CO_2 from being emitted into the atmosphere, and thus play a major role in significantly reducing greenhouse gas emissions.

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EXECUTIVE SUMMARY

Air Products commercially operates two industrial steam methane reformers at a Port Arthur, Texas site which provide a concentrated CO_2 stream. This CO_2 stream generated in Air Products' Commercial Operations is captured using a large-scale industrial carbon capture system in which the concentrated CO_2 stream is purified, dehydrated and compressed (PDC Activities) to form a CO_2-enriched stream. The objective of this large-scale industrial carbon capture and sequestration (CCS) project is to demonstrate that such commercially-operated advanced technology embodied in Air Products' Commercial Operations can successfully capture carbon dioxide (CO_2) emissions from industrial sources.

The Department of Energy (DOE) objective is to demonstrate, at commercial scale in an industrial setting, technologies that 1) make progress toward capture and sequestration of 75% of the CO_2 from the treated stream composed of at least 10% CO_2 by volume that would otherwise be emitted to the atmosphere, and 2) are at a scale sufficient to evaluate the full impact of the CO_2 capture technology on industrial plant operations, economics, and performance. The DOE's target was for the project to capture amounts of CO_2 approaching one million tons per year by 2015 as an integral component of commercial operation.

Denbury Onshore is commercially engaged in enhanced oil recovery (EOR) projects and currently operates 16 CO_2 EOR projects and a natural source of CO_2. Denbury Green Pipeline owns and operates the Green Pipeline, which was developed at private expense. Separate from the cooperative agreement, Air Products entered a commercial contract with Denbury Onshore for Denbury Onshore to purchase the CO_2-enriched stream produced by Air Products for use in the West Hastings Unit EOR Project. In addition, under a separate commercial contract with Denbury Green Pipeline, Air Products ships the CO_2-enriched stream produced by Air Products on the Green Pipeline to the West Hastings EOR Project. These commercial contracts, as well as Denbury Onshore's commercial EOR operations and Denbury Green Pipeline's commercial pipeline operations, fall outside the scope of the cooperative agreement for this project. These related commercial operations are the basis for Denbury Onshore to conduct a research program to monitor, verify and account (the "Research MVA Activities") for such CO_2 in order to demonstrate the efficacy of CO_2 sequestration through EOR.

The project was conducted in two distinct phases. The overall objective of Phase 1 was to develop a fully definitive project basis for a competitive renewal application process to proceed into Phase 2 - Design, Construction and Operations. Specific Phase 1 objectives included development of 1) a firm project baseline of PDC Activities and Research MVA Activities; 2) a detailed project management plan; 3) a definitive project schedule; 4) a definitive project cost estimate; 5) firm host site and subcontracting commitments; 6) firm financial commitments and funding plans for the non-Federal share of the project costs; and 7) applicable environmental permitting and National Environmental Policy Act (NEPA) activities.

The overall objective of Phase 2 was to design, construct and operate the project for the purpose of demonstrating the performance of the PDC and Research MVA Activities relative to the DOE goals and objectives. Phase 2 has three sub-phases: Sub-Phases 2A and 2B, associated with Project Management, Engineering and Procurement and Construction and Commissioning; and Sub-Phase 2C, associated with Operations and Maintenance of the PDC. The PDC was put on-stream in December 2012 and achieved full production in March 2013.

A CO_2 capacity test, conducted 6-7 May 2013, demonstrated that the PDC can, on an instantaneous basis, achieve the rate of CO_2 production commensurate with the DOE's goal to capture amounts of CO_2 approaching one million tons per year. Further, the testing demonstrated that PDC performance can exceed the DOE's goal to capture 75% of the CO_2 from a treated stream composed of at least 10% CO_2 by volume that would otherwise be emitted to the atmosphere.

PHASE 1 (16 NOVEMBER 2009 - 16 JUNE 2010)

In Phase 1, Air Products and Chemicals, Inc. (Air Products), along with project partners including the URS Group, developed the most cost-effective CO_2 removal technology for integrated SMRs. This application was initially based on a methyl-diethanolamine (MDEA) recovery system. It was believed that MDEA, a commercially proven and readily available liquid absorption technology, would provide the lowest cost per ton of CO_2 removed from the Port Arthur SMRs. Different adsorption, absorption, and cryogenic technologies were evaluated.

Purification, Drying and Compression (PDC)

Phase 1 provided a greater understanding of this integrated SMR opportunity. It was determined that capturing the CO_2 via vacuum swing adsorption (VSA) would provide a more optimal solution based on lower operating costs and projected capital.

Several major factors led Air Products to select a VSA technology as the basis for moving forward in the Phase 2 application. First, the Port Arthur SMRs are non-traditional in the sense that they are highly integrated with steam/gas turbines and a heat recovery steam generation unit. This level of integration allows Air Products to produce hydrogen, steam, and power more efficiently than if these products were produced individually. Compared to other technologies, the initially proposed MDEA system requires more steam for the regeneration of the solvent used in the absorption process. While this level of energy can be readily captured in less integrated SMRs, it is not available with an integrated SMR without a significant impact to export steam that is contractually obligated to be made available. Third, after detailed analysis, it was concluded that the VSA recovery solution provided the lowest overall cost per ton of CO_2 captured at the Port Arthur facilities.

In addition, Air Products prepared an Environmental Information Volume (EIV) to summarize the potential environmental, safety, health, and socioeconomic impacts associated with Air Products' proposed Port Arthur carbon capture and sequestration (CCS) project. Potential risks associated with the project were anticipated to be minimal. Because the areas on which the process facility was to be constructed had been previously used for industrial purposes, there was potential for drilling or excavation activities to encounter unknown underground utilities or soil/groundwater impacted from prior activity at the site. Air Products mitigated these risks using their best management practices (BMPs) for underground clearance prior to drilling or excavating. Liability in this event would be limited to a construction delay and additional environmental evaluation while Air Products worked with the site owner and any other affected parties to resolve the issue.

The CO_2 from the H_2 product raw gas streams at each Air Products SMR/H_2 facility would be removed using identical Air Products proprietary VSA technology. The VSA systems were to be engineered, designed, procured and constructed by Air Products. The CO_2 recovery from both Air Products facilities was estimated to capture and sequester approximately one million (1MM) metric tons per year that would otherwise be released to the atmosphere.

It was determined that the CO_2 recovery, drying, and compression would reduce steam-making capacity at both Air Products SMR/H_2 facilities and utilize additional power. To maintain the same overall utility and product balance, the project included the addition of a COGEN system comprising a gas turbine generator (GT) and heat recovery steam generator (HRSG).

The Port Arthur 1 facility (PA1), brought on-stream in 2000, supplies over 100 MM standard cubic feet per day (SCFD) of on-purpose hydrogen to the Air Products West Gulf Coast (WGC) hydrogen pipeline. This innovative SMR/cogeneration facility utilizes the waste heat from a combustion turbine to provide the process heat needs for the SMR, while simultaneously producing 40 MW of power and greater than 500,000 lbs/hr of steam for the site host in addition to the on-purpose hydrogen. The plant was designed to operate under various modes for maximum flexibility and reliability (modes include both integrated and non-integrated, which means that while the major process units are designed to operate together, they can function independently). The feedstock for this facility is natural gas, which is converted in the SMR using steam over a catalyst to produce hydrogen. The raw hydrogen is purified to pipeline specification via a PSA system, then compressed for delivery to Air Products' WGC customers via the pipeline. This facility was designed and executed under the Air Products/Technip alliance.

In September 2006, Air Products commissioned a second SMR (PA2) at the same Port Arthur site capable of producing over 100 MMSCFD of hydrogen, ~100 MW of power, and ~1,000,000 lbs/hr of steam. This first-of-a-kind SMR/cogeneration facility was again designed and executed under the Air Products/Technip alliance. The PA2 facility utilizes the exhaust from an even larger combustion turbine to provide process heat needs for both the SMR and also a separate HRSG.

Table 1. Air Products' Phase 1 accomplishments.

• Completed technology selection review. o The analysis concluded that the VSA technology was the most applicable when compared to amine-based and cryogenic-based CO_2 removal technologies for this opportunity based on the lower projected capital and operating costs. The VSAs will allow Air Products to capture and sequester over 1 MM TPY.
• Completed capital estimate for CO_2 recovery system including the co-gen unit – approximately $300,000,000
• Completed utility, operations and maintenance cost estimate - approximately $150,000,000
• Project Management Plan completed o Included a Resource-Load Schedule
• Estimate Planning/Scoping completed o Completed schedule developed; see Phase 2 Schedule summary (p. 34) for actual performance o Project scope defined o Completed detailed discussions with host site in order to develop project scope and feasibility
• Process Work o Aspen simulations of both SMRs with/without CO_2 capture for selected cases are completed: ▪ These simulations were necessary to determine the adequacy of certain existing equipment ▪ Current ID fans are adequate in the CO_2 capture simulations ▪ Pressure Swing Adsorption (PSA) hydrogen recovery does decline, but it will still be deemed to be adequate ▪ Completed process work to fully understand how SMRs and CO_2 capture equipment will function together and independently

Table 1. Air Products' Phase 1 accomplishments. (cont.)

• Process Work o Completed process equipment specifications for major new items that will be required due to new operating conditions ▪ Burners ▪ SCR ▪ VSA vessels ▪ CO_2 compression o Vendor contacts completed (burners, SCR, drying, compression, VSA vessels) o PFD modifications completed • Tie-in lists, P&ID, Utility completed
• Environment planning for Phase 2 completed o Continued discussions to determine low-cost utility supply
• Furthered detailed Denbury Onshore negotiations concerning off take agreement
• Furthered discussions with the host site to determine low-cost supply of utilities
• Developed detailed plot plans

Monitoring, Verification and Accounting (MVA)

Denbury Onshore was responsible for the Research MVA scope of this project. At this stage, existing conditions at the West Hastings Unit were typical for a mature and historically productive oil and natural gas field. Denbury used available information to avoid waste management areas and utilities located at the site. If unexpected waste or utilities were encountered during drilling, the test well was to be relocated with minimal delay. The possibility of the leakage in the West Hastings location was extremely remote due to the extensive configuration of geologic seals that separate the deep injection formations from shallow local aquifers and the surface.

Denbury's Regulatory Compliance Team is experienced with large-scale EOR and other oil and gas enterprises. Given the small scale of permitting and regulatory issues related to the Research MVA Activities, Denbury's compliance team encountered few environmental issues outside their routine permitting and oversight duties.

Phase 1 Conclusions

During Phase 1, Air Products conducted an extensive review to determine the low-cost method of removing CO_2 from its integrated SMRs in Port Arthur, TX. The analysis concluded that the VSA technology was the most applicable for this opportunity based on the lower projected capital and operating costs.

CO_2 Plant Major Process Units

VSA Process Description

A CO_2 removal unit utilizing Air Products' CO_2 VSA technology was retrofitted to each of the two existing SMR trains at the Air Products Port Arthur hydrogen complex as described below. Each VSA unit is designed to remove >90% of the CO_2 contained in the reformer PSA feed gas. "Sweet" syngas (CO_2 removed) returns from the CO_2 VSA system and feeds the existing SMR H_2 PSAs. Offgas from the exiting H_2 PSAs changed in flow and composition, so a modification was required for all existing burners at the two SMRs. CO_2 produced off the VSA units is compressed and dried in a single train located at PA2. A cogeneration unit was installed to supply energy to the VSA and SMR plants. Additional details are discussed below.

VSA System

Cooled CO_2-containing syngas from the SMR cold process condensate separator is routed to the VSA system. The CO_2 contained in the process gas of the PA1 and PA2 SMRs is removed with multiple VSA units, each of which includes a series of vessels filled with adsorbent to selectively remove one or more components from the feed gas. In this case, the feed gas is the raw hydrogen stream from an SMR plant upstream of the existing hydrogen PSA. Generally, the VSA cycle is similar to Air Products' hydrogen PSA cycle. Adsorber vessels are fed with gas at ~400 psia, causing selective adsorption of feed components, specifically CO_2, onto the adsorbent bed. The gas not adsorbed by the bed is a hydrogen-rich stream that is sent to the H_2 PSA for further purification. Then, the vessel undergoes a series of pressure equalizations with vessels at lower pressures before a CO_2 product is drawn off. There are two unique steps in the VSA cycle to produce a CO_2–rich stream of high purity. In the first step, a vacuum pump draws off the CO_2 product to sub-atmospheric pressures in an "evacuation" step. The other is a "rinse" step in which blowdown gas is taken from an intermediate pressure bed, compressed, and fed to a higher-pressure bed. While the "rinse" and "evacuation" steps are the keys to achieving a high-purity CO_2 product, they also consume power.

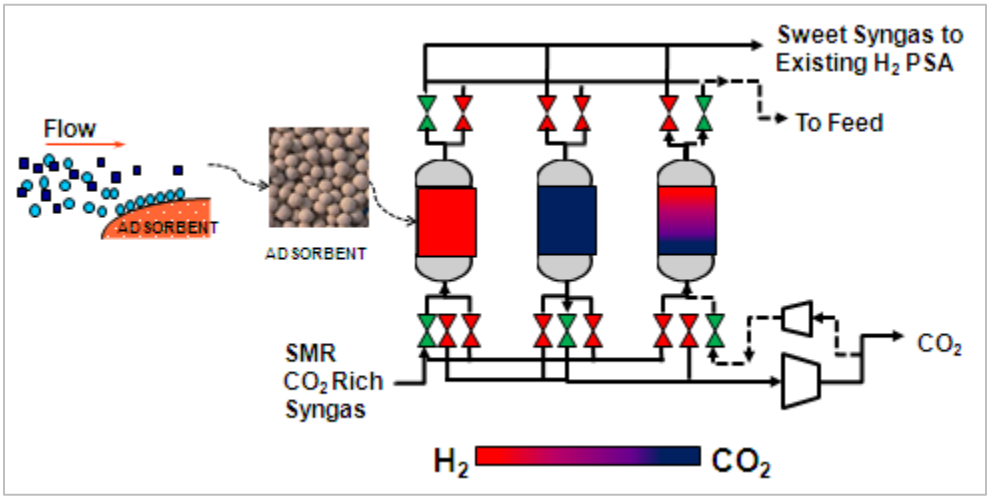

Figure 1. VSA CO_2 process.

Steam Methane Reformer Operation Including Process Gas CO_2 Removal

The majority of the fuel fired in a hydrogen plant steam methane reformer is purge gas from the PSA hydrogen purification unit. The purge gas consists of essentially all the impurities contained in the shifted reformer effluent plus unrecovered hydrogen. The major component in the purge gas is CO_2, which is typically present at a concentration of ~45 volume percent. Removing this component from the stream reduces the volumetric flow through the burners, increases adiabatic flame temperatures, and requires that some process operating conditions change.

The SMRs at Port Arthur utilize gas turbines and maximize steam production in a highly integrated design. Reduced CO_2 concentration in the purge gas to the SMR burners results in lower mass flow through the SMR convection section. As a result, the SMR produces less steam. This steam loss was made up by the addition of a new cogeneration unit which was used to produce power and capture the resulting waste heat to generate steam.

The SMR burners for both hydrogen plants were evaluated and modified for future operation with CO_2 removal. This change is due to the fact that CO_2 makes up a large portion of the purge gas. When the CO_2 is removed, the pressure drop in that circuit changes.

The existing SMRs utilize selective catalytic reduction (SCR) catalysts to control NO_x emissions. SCR is a catalytic flue gas system which converts ~90% of the flue gas NO_x. The emission profile from the burners will change with CO_2 removal. Removing the CO_2 results in higher adiabatic flame temperatures, which translates to higher NO_x emissions. This will result in an increased frequency of SCR catalyst change outs over the life of the facility. Ammonia consumption in the SCR will increase by 2-3 times their current levels.

One goal of this project is that operation with the new equipment have a minimal impact on hydrogen production. Instrument and control logic was implemented to maintain operation of the reformer and PSA in the event of an upset or trip of the VSA unit. Loss of the VSA unit operation results in a sudden increase in the CO_2 content and flow of the PSA feed, and therefore in the PSA purge gas going to the burners. On a sudden switch, this increase in purge gas flow is accounted for in the control logic, which automatically adjusts the PSA operation and sends a portion of the purge gas to the flare during the transition until the problem is resolved. A full flow bypass was installed around the VSA with an automatic valve which provides the normal flow path to the PSA when the CO_2 plant is down for any reason.

CO_2 Compressor and Dryer Systems (PA2 Site)

Raw CO_2 exits the two trains of the VSA systems after cooling and is combined at the suction of the first stage of the compressor, which is an eight-stage, integrally-geared centrifugal compressor. The compressor is driven by a ~12 MW electric motor. Each of the first five compressor stages is followed by an intercooler, which also includes an integral separating section to remove condensate, which is mostly water. The CO_2 compression first stage suction pressure is ~16 psia. The fluid for the coolers is supplied from a new cooling tower. Condensate from the first five intercoolers is combined in a common vessel and piped to the existing plant waste sump.

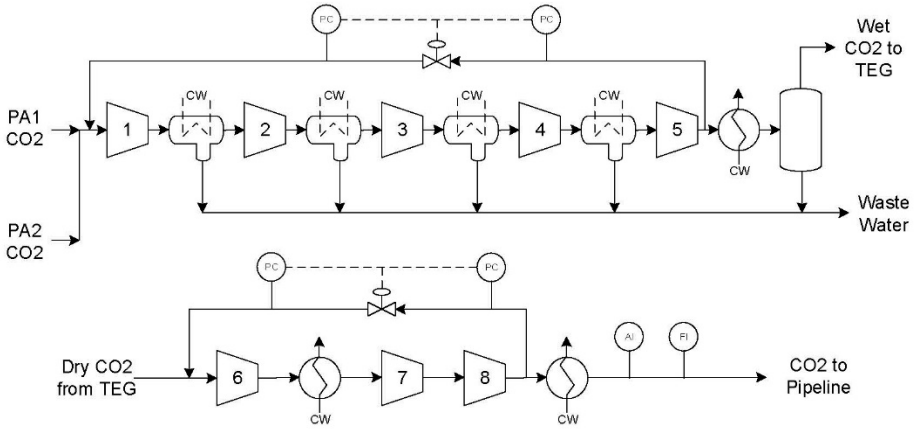

Figure 2. CO_2 compressor.

CO_2 exiting the Stage 5 intercooler is sent to a triethylene glycol (TEG) drying system, where water is removed. After drying, the CO_2 is sent to the Stage 6 suction, where the final compression

occurs in Stages 6, 7 and 8. After final cooling following Stage 8, the CO_2 exits the battery limits and enters the CO_2 pipeline at the required pipeline pressure (2200 psig).

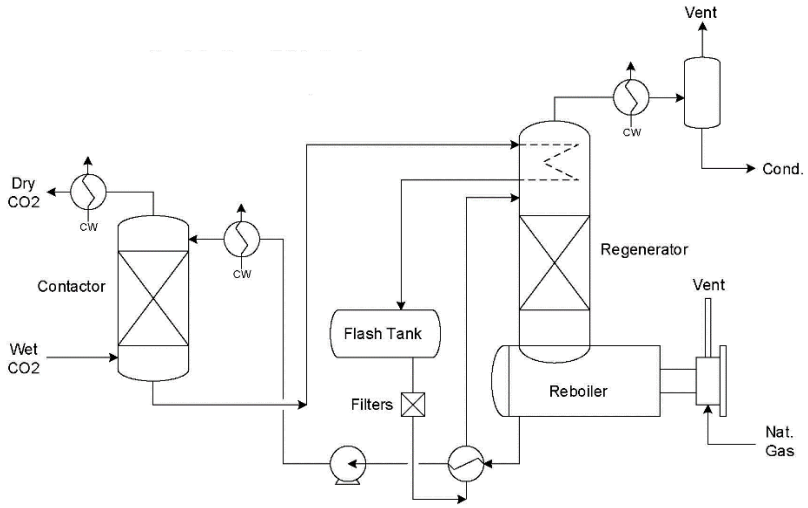

Figure 3. TEG dryer unit.

The function of the TEG dehydration unit is to remove water vapor from the wet, compressed CO_2 stream to an outlet water content meeting pipeline specifications, here defined as <30 lb/MMscf. TEG dehydration units have routinely been used for CO_2 dehydration for enhanced oil recovery applications, as well as being the standard technology for natural gas drying. TEG has a very high affinity for water, allowing very high removal, and a low volatility, minimizing solvent losses into the CO_2 product.

The wet CO_2 exits the after cooler following Stage 5 compression and is contacted with lean, dry TEG in the tray or structured packing section of the contactor tower, where water vapor is absorbed in the TEG, thus reducing its water content to less than 30 lb/MMscf. The dry CO_2 exiting the top of the absorber is sent to the final three stages of CO_2 compression, where the CO_2 is raised above the critical pressure of 1071 psia. The glycol content of the dry CO_2 is very low.

The wet, rich TEG exiting the contactor is depressurized and flows to the regeneration system. The wet, rich TEG is pre-heated and flashed in a horizontal separator to remove much of the dissolved CO_2 and other light gases. The flash gas is sent back to the compressor so that the contained CO_2 is not lost. The flashed water-rich TEG liquor is cleaned in charcoal and sock filters and then heated with lean TEG from the regenerator column. The rich, heated TEG is then fractionated in the regenerator column and by heating in the reboiler and boiling off the absorbed water vapor. The lean glycol exiting the bottom of the regenerator is cooled with rich TEG and pumped back to the absorber. The reboiler is directly fired with natural gas. The overhead vapor from the regenerator column, consisting primarily of CO_2 and water vapor, is cooled to knock out trace levels of methanol, and then vented to atmosphere; glycol content in this vent stream is low, estimated at 0.06 lb/hr.

The only utilities required by the dehydration system are small amounts of natural gas and power for the recirculation pump. Small amounts of make-up glycol are required periodically; drum supply is adequate after the initial fill. The only effluents are the flash gas and regenerator overhead vapor streams; there are no liquid effluents.

Gas Turbine and HRSG System

A ~21 MW gas turbine and a 100Mlbs/h medium-pressure HRSG was installed to provide:

- Power for the new PA1 and PA2 CO_2 system loads, and
- 650 psi steam to make up for SMR steam production losses due to removal of CO_2 in the SMR flue gas

The gas turbine size was selected to produce the additional power required for the new CO_2 capture equipment and the HRSG sizing was based on replacing the steam production that is lost as a result of removing the CO_2 from the process stream. Total fuel requirements are ~270MMBtu/hr-HHV when producing 21,535 net KW at average ambient temperature and new/clean conditions. An SCR system for NOx control was installed on the HRSG stack.

CO_2 CAPTURE TECHNOLOGY DEVELOPMENT

TECHNOLOGY FOR CO_2 SEPARATION FROM SYNGAS

General Background

Separation of carbon dioxide (CO_2) from a syngas stream has been widely practiced in industry for decades. Common examples of this include production of ammonia, hydrogen, and carbon monoxide. Technologies which have been developed for this separation fall into two broad categories, absorption and adsorption.

Absorption-Based Technology

Absorption-based technology uses a chemical or physical solvent to remove acid gas from syngas or other gas streams. A multitude of solvents have been used in the industry; some of the most common are listed below.

Chemical Solvents	Physical Solvents
Primary amines: MEA	Chilled methanol
Secondary amines: DEA, DGA	Dimethylether of polyethylene glycol
Tertiary amines: MDEA	Diisopropanol amine + sulfulane
Alkali salts: Potassium carbonate, sodium hydroxide	

The solvents that have been commercially developed and employed in the industry have their relative merits based on the following: the type of gas stream being treated, the contaminants in the stream, the level of CO_2 and other acid gas in the gas stream, the amount of acid gas removal required, the desire for separation of individual acid gases, and economic evaluation factors.

Figure 4 shows a typical absorption process diagram for CO_2 separation from syngas.

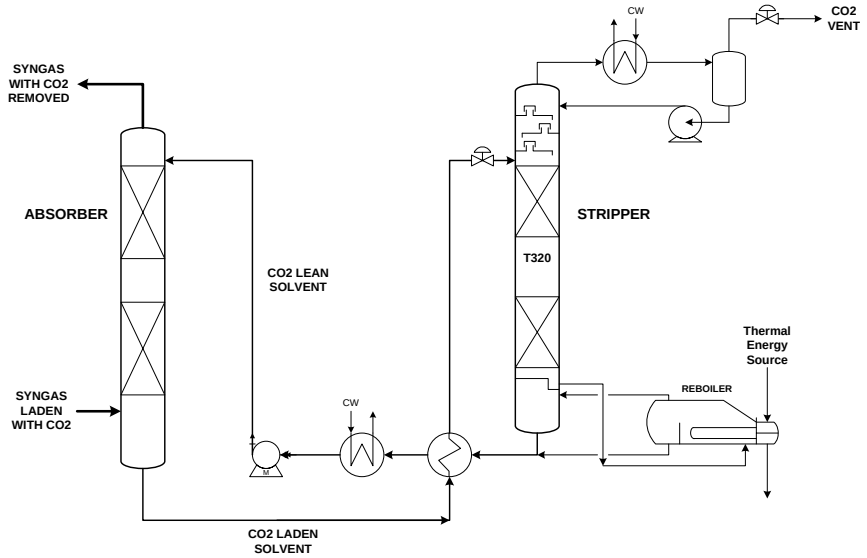

Figure 4. Typical absorption process diagram.

The main principal of operation is that CO_2 is selectively adsorbed by the solvent at higher pressure and lower temperature in an absorption column, and is then removed from the solvent at lower

pressure and high temperature in a stripper column. The solvent circulates in a closed loop between the two columns. Several design features can be added to the process (e.g., flash drums, additional columns and heat exchangers, and solvent conditioning equipment) to enhance the overall performance of the system. Thermal energy is required to operate the stripper column reboiler and constitutes the main operation cost. Energy consumption can range from 15,000 to 75,000 Btu/lbmol CO_2 depending on the level of CO_2 removed, solvent selection, and design features added to improve energy efficiency.

Amines (primary, secondary, and tertiary) have been most typically used for separation of CO_2 from syngas where there are no other acid gases and CO_2 recovery is desired. An example of separation and recovery of CO_2 from a syngas stream via an amine-based absorption process is the production of beverage-grade CO_2. There are numerous examples of this type of process throughout the world (see Figure 5). Production levels from these units are usually on the order of hundreds of tons per day to support a regional market for beverage-grade CO_2. Air Products previously operated a facility like this in New Orleans from the 1970s to 2003.

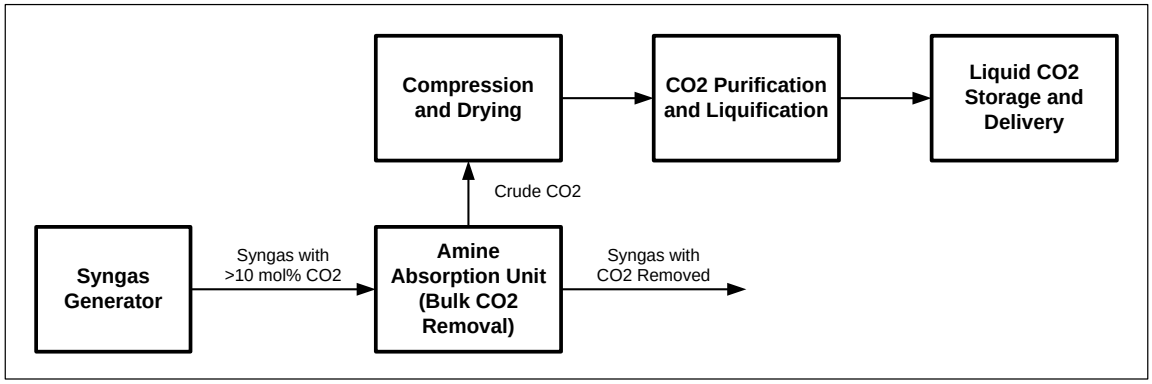

Figure 5. Process block diagram for production of beverage-grade CO_2 from syngas.

Adsorption is the selective transfer of one or more chemical compounds to solid particles (an adsorbent). The selectivity of an adsorbent between different adsorbed compounds makes it possible to separate compounds from one another. Adsorption takes place on the solid surface; therefore, a material that exhibits good adsorptive properties must have a large surface area relative to its volume. Most of this surface exists as pores within the solid particles. Adsorption is usually caused by intermolecular forces, such as Van der Waals forces or polar attractions, rather than by chemical reaction. If there is transfer of electrons between the adsorbed compound and the adsorbent, it is termed chemisorption.

Adsorption processes are generally non-continuous. The gas is allowed to contact an adsorbent, usually in a fixed bed, until the adsorbent is saturated with adsorbate. The product gas can be in either the adsorbed phase or the non-adsorbed phase, depending on the process. The adsorbent is then taken off line and regenerated before used again for further adsorption. Several beds must be used to process a continuous flow of gas, with some beds in adsorption and the remainder in regeneration steps. The switching between beds as they alternate between adsorption and regeneration produces some irregularities in the flows of both the adsorbed and non-adsorbed streams. If the adsorption cycle is long, this is usually not an issue. For shorter cycles, dampening these irregularities is more critical.

Figure 6 illustrates an adsorption process consisting of eight separate beds designed to have one bed on feed, three pressure equalizations (6 beds total) for transitioning from the adsorption to regeneration steps, and one bed on regeneration where the adsorbate is recovered. The feed gas is switched from one bed to the next while the beds simultaneously progress through this sequence of adsorption-transition-regeneration steps.

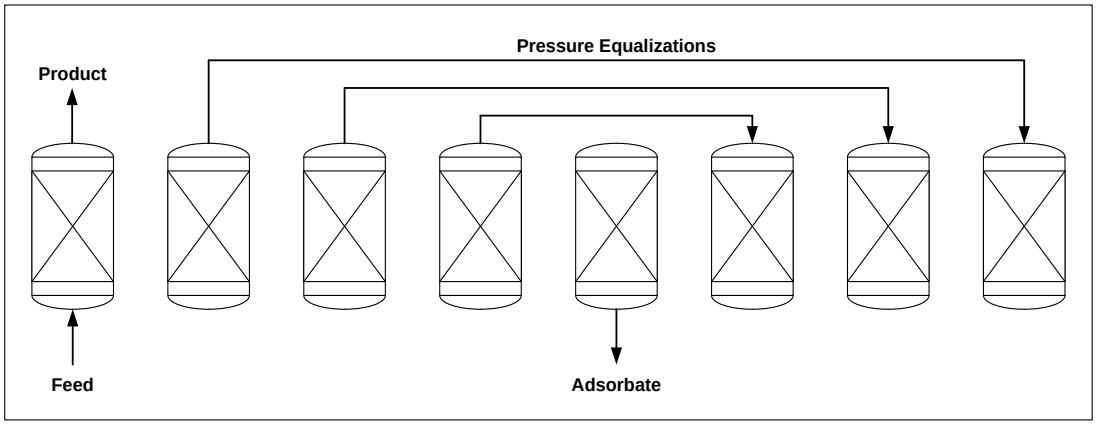

Figure 6. Typical absorption process diagram.

Since adsorption is exothermic, adsorbate removal can be effected by either adding heat to the system or by changing the system such that the energy contained by the adsorbent and adsorbate is sufficient to remove the adsorbate from the particle. This can best be explained by illustrating an isotherm. An isotherm is used to describe how much of a particular material can be adsorbed on a solid at a constant temperature as a function of that component's partial pressure in the gas phase contacting the adsorbent particle.

Figure 7 shows two isotherms for a given gas/adsorbent pair. Each curve shows the equilibrium pickup of the gas at a given temperature for a range of gas partial pressures with $T_2 > T_1$. Point 1 represents an adsorbent fully saturated with the gas at a given pressure and temperature. To remove this gas from the adsorbent, the temperature can be raised from T_1 to T_2. This is represented by path A on the chart. More gas can be removed by reducing the pressure as temperature is increased (path B). Using temperature to regenerate an adsorption process is termed a temperature swing adsorption (TSA) process.

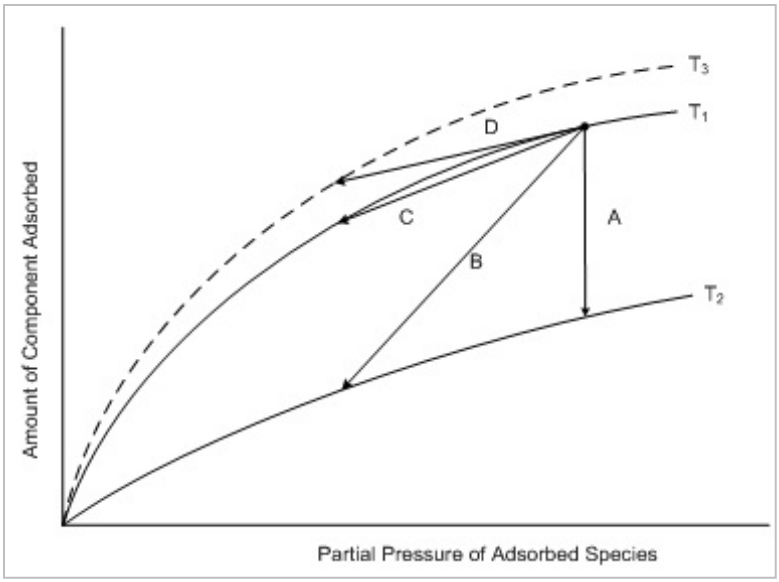

Figure 7. Adsorption isotherms.

If the bed is regenerated isothermally using path C by depressurizing to a lower pressure where less gas can be held on the adsorbent (no external heat is applied), then the process is termed a pressure swing adsorption (PSA) process. The low pressure level for both paths B and C is at about atmospheric pressure. As seen in the simplified diagram, this will leave more adsorbate on the adsorbent for the PSA process. As a result, the working capacity of the adsorbent is less in a PSA cycle than it would be if used in a TSA cycle.

In reality, it is impossible to regenerate a bed isothermally; the best that can be done in the real world is maintaining it as adiabatic. Adiabatic depressurization will cool a bed so that $T_3 < T_1$. T1 is the adsorption temperature of the bed and the resultant desorption route for this case is shown as path D.

The preferred adsorption processes to use is determined by the specific application. A TSA is generally used when a relatively dilute, strongly-adsorbed impurity such as moisture or CO_2 must be removed. In these cases, an adsorber can be on stream for a long period (4-16 hours) which provides the time needed to heat and cool the vessel to regenerate the adsorbent.

As the flow rate and amount of impurity rises and/or the amount of impurity that can be adsorbed by the adsorbent decreases, very large bed sizes are needed to purify the gas stream within the required TSA cycle times. Under these conditions, a PSA cycle provides advantages (even with the lower adsorbent working capacity described above) due to the ability to change pressures more rapidly than temperatures. Cycle times for PSA processes are generally measured in minutes or even seconds, rather than the hours required by TSA processes.

There are several variants of each basic cycle. For instance, a true TSA has no pressure variation between the adsorption and desorption steps. If the bed is depressurized before regeneration heat is applied, it may be called a PTSA, with the P denoting that the pressure is varied during the cycle along with the temperature. Similarly, if the regeneration pressure is below atmospheric, the cycle may be termed a VSA or VPSA, where in both cases the V stands for vacuum.

Adsorbent processes to remove CO_2 from syngas have generally been practiced in industry in two ways. When producing hydrogen from a syngas stream, a PSA process is used to remove CO_2 and nearly all of the other gas components in the syngas from the hydrogen. This separates CO_2 from hydrogen but not from the other gas components such as methane, carbon monoxide, nitrogen, and water (Figure 8).

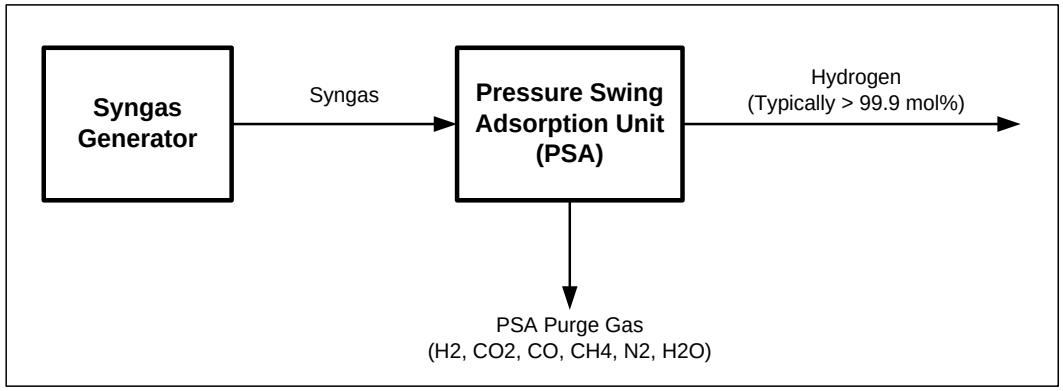

Figure 8. Application of PSA adsorption for purification of syngas.

In cryogenic separation of syngas into hydrogen, carbon monoxide, and/or syngas products, a TSA process is used to remove low levels of CO_2 and water from the syngas after bulk removal of CO_2 (Figure 9). However, in this case, the amount of CO_2 is very low (<1 ton per day) and the CO_2 is not recovered as a pure stream but instead picked up by another gas stream used to thermally regenerate the adsorbent.

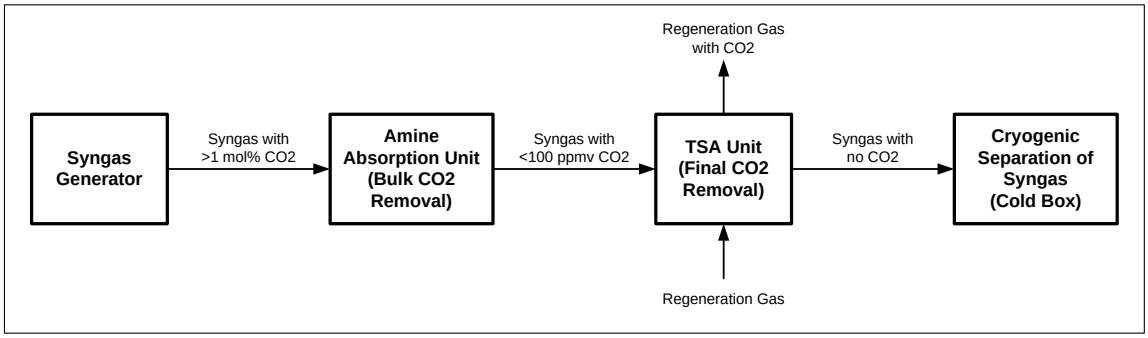

Figure 9. Application of TSA adsorption for cryogenic purification of syngas.

Recovery of nearly pure CO_2 from syngas via an adsorption process is not commonly practiced in industry. Air Products has performed this separation in a commercial unit in a hydrogen production plant in Butler, Pennsylvania. This plant has been in continuous operation since it was brought on-stream in 1986. The CO_2 is separated from the syngas for the original purpose of selling it as a product, but the demand for it never materialized. A basic diagram of this process is shown in Figure 10. A unique aspect of this design is the level of integration between the VSA process, which separates the CO_2 from the syngas, and the PSA process, which generates the H_2 product. Multiple gas streams are exchanged between these two process units.

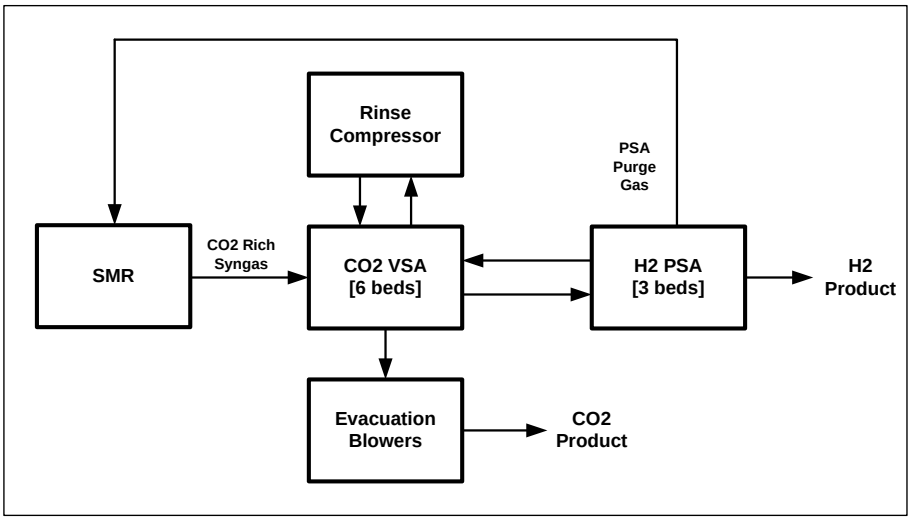

Figure 10. Process block diagram of Air Products' Butler, PA plant.

AIR PRODUCTS ADSORPTION TECHNOLOGY DEVELOPMENT CAPABILITIES

Overview

As a leading industrial gas company, Air Products must develop new technology to support the businesses in which we are active. Air Products has been developing adsorption-based gas separation technologies for several decades, work which includes a broad-based focus to gain a fundamental understanding of adsorption. Examples of this include measurement of reversible and irreversible adsorption capacity over large temperature and pressure ranges via volumetric, gravimetric, and isotope exchange techniques; measurement of multi-component adsorption capacity; adsorption calorimetry; measurement of mass transfer characteristics via breakthrough, uptake and zero-length chromatography (ZLC) techniques; and development of mathematical models to describe to physical interactions between adsorbates and adsorbents.

Some development work has been very focused on specific applications which satisfy particular needs or opportunities in the industrial gas market. Examples of this include purification of hydrogen from both steam methane and autothermal reforming offgas, coal gasification processes, chemical process offgas, and refinery fuel streams; purification of oxygen or nitrogen from air; removal of carbon dioxide and water from air for cryogenic processing; upgrading methane from landfill gas, coal bed gas, biogas, and pipeline gas; purification of nitrogen from monomers released in polymer purge processes; purification of helium from nitrogen; and methane in helium recovery processes.

Air Products has been granted over 250 patents since 1990 related to gas separation via adsorption, illustrating our commitment to and capabilities in this area of technology development.

Specific Capabilities

To support technology development of adsorption processes, Air Products has both a pilot-scale testing unit and a computer-based modeling tool at its offices in Trexlertown, Pennsylvania.

Pilot Unit for Adsorption Technology Development

The pilot unit allows controlled experiments of an adsorption process to be conducted to obtain measured results of performance. The unit consists of multiple columns which can hold one or more adsorbents, feed gas flow controllers which can blend several gases to simulate a feed gas stream, valve manifolds which allow pressure equalizations between two or more columns, instruments and analyzers to measure process parameters, and a computer-based control and data acquisition system. This pilot unit has been in use at Air Products' corporate and R&D headquarters in Trexlertown since 1992.

Computer-Based Modeling Tool

The computer-based modeling tool uses nonisothermal, nonlinear, nonequilibrium and nonisobaric models to simulate pressure and vacuum swing adsorption cycles. The partial differential equations which describe the mass, momentum and energy balances within the column are numerically discretized and solved by dividing the column into nodes representing from one to six inches of adsorbent height. Features of the simulator include the ability to model the effect of multiple adsorbents in an adsorbent bed, the flexibility to describe multiple processing steps, and the capability for the user to choose from a variety of models for adsorption isotherms and rate processes. The adsorption process simulator considers the adsorbent to be radially uniform and assumes that all columns are identical. This simulation program has proven to be useful in the

development of efficient adsorption processes. Its utility has been demonstrated through the design and optimization of several commercial scale-installations.

SEPARATION TECHNOLOGY SELECTION & DEVELOPMENT FOR PORT ARTHUR CO_2 CAPTURE PROJECT

Initial Technology Selection and Development Work

In Phase 1 development work in late 2009, Air Products had selected an amine-based CO_2 separation technology to integrate into the Port Arthur CO_2 capture project. The specific amine to be used was BASF's activated MDEA (aMDEA) technology, which has been widely used to separate CO_2 from syngas (and other gas streams). At the time, Air Products had a basic process modeling tool for the technology which allowed performance evaluation and design studies to be completed to support cost estimates and project development.

Due to the relatively high value of thermal energy at the Port Arthur SMR plants, considerable effort was undertaken to maximize the thermal energy efficiency of the aMDEA design. Air Products evaluated a dual absorption column design which minimizes the thermal energy usage by employing a semi-regenerated amine solution. Figure 11 depicts this design.

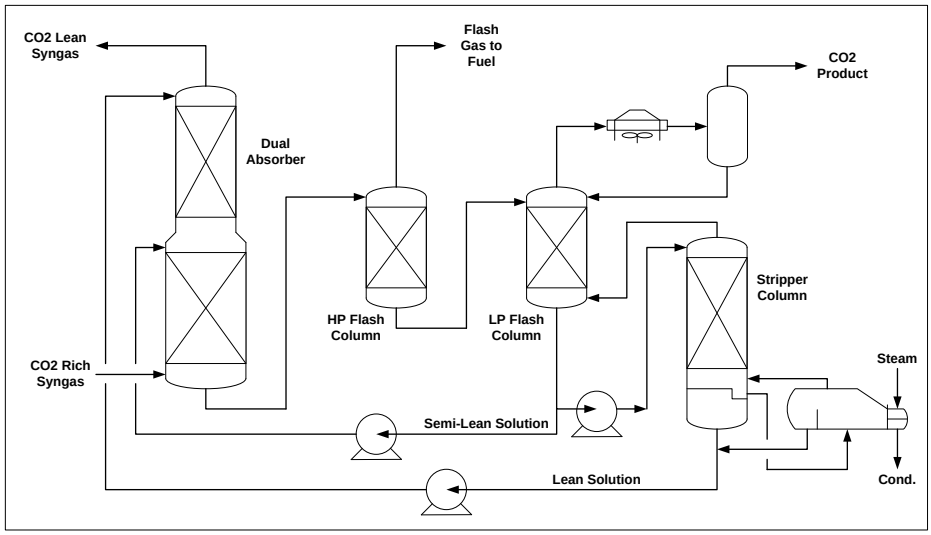

Figure 11. BASF's design for CO_2 removal using an aMDEA dual absorption column.

The unique feature of this process is that CO_2 removal from the syngas in the absorber is achieved by first contacting the syngas with a semi-lean solution which has ***not*** been thermally regenerated, then contacting it with a lean solution which ***has*** been thermally regenerated. This greatly reduces the thermal energy required to capture the CO_2, but at the expense of significantly increasing the solution circulation rate and the need to add more and larger equipment.

Specific thermal energy consumption was in the range of 0.75 to 1.0 MMbtu/short ton of CO_2. While this is a very good thermal efficiency for an absorption-based CO_2 capture process, the resultant loss of steam production and economic efficiency in the SMR process was notable and presented a barrier for advancing the project.

In early 2010, Air Products started to consider vacuum swing adsorption as an alternate technology for CO_2 capture at Port Arthur. At the time, vacuum swing adsorption technology was in its early

stages as engineering study and was not ready for immediate use in an actual project. Preliminary process design work to determine a basic VSA cycle had been completed, but several other areas of basic engineering development were lacking. These included:

- Validation of the process design model and basic thermodynamic properties
- Development of equipment designs for the vacuum blowers and rinse compressors
- Identification of qualified vacuum blower suppliers for this large-scale application
- Development of Piping and Instrumentation drawings (P&IDs) to define basic operational, reliability, control, and cost aspects of the technology

The starting point for CO_2 recovery from the SMR effluent by adsorption was an eight-bed cycle that included typical steps employed to separate gases from a high-pressure stream: adsorption at high pressure; several concurrent depressurization steps; rinse; countercurrent depressurization (blowdown); evacuation; and several countercurrent repressurization steps. Because the adsorbent is highly selective for carbon dioxide, the evacuation step recovers a stream highly enriched in CO_2. The rinse step, which allows the CO_2 concentration in the adsorber vessels to reach very high levels, uses gas recovered during countercurrent depressurization. The combination of these two steps (blowdown and rinse) acts as a reflux to increase the CO_2 content in the column, sweeping out the unwanted, less-adsorbed impurities.

Though Air Products had built and operated CO_2-VSA-based processes in the 1980s (notably the previously mentioned Butler, PA unit in 1986), these systems were established before computer models of adsorption processes were fully developed for plant design purposes. A connection between process performance, adsorbent characterization, and model prediction had not yet been identified. The adsorption characteristics of several CO_2-selective adsorbents had been measured and modeled, but not tested for use in CO_2 recovery processes.

Initial work determined the sensitivity of adsorption model parameters to predicted performance. Adsorbent parameters obtained for several similar CO_2-selective adsorbents were used to determine expected performance and equipment requirements under identical conditions of feed flow rate, VSA cycle time, evacuation pressure, and product purity. Because many of these adsorbents were considered equivalent at this point, this exercise was intended as a sensitivity test, not an effort to identify a preferred adsorbent. The adsorbent parameters that resulted in the most conservative design requirements were chosen for further study.

The potential of the eight-bed CO_2-VSA cycle for recovery of carbon dioxide from the high-pressure SMR effluent was investigated by extracting the predicted relationship between vacuum level, adsorbent quantity and carbon dioxide recovery at a fixed product purity of 98% CO_2. This study confirmed that >90% of the CO_2 could be recovered, which would enable up to 1 million tons per year of CO_2 to be captured at Port Arthur, the minimum target for the Port Arthur CO_2 capture project.

In March 2010, Air Products compared the aMDEA and VSA technologies to determine which would be dropped from further consideration for the Port Arthur CO_2 project. This evaluation yielded a decision not to pursue the aMDEA technology mainly due to operating cost disadvantages. For the remainder of the Phase 1 development work, Air Products focused solely on development of the VSA technology.

PHASE 2 (17 JUNE 2010 - 30 SEPTEMBER 2017)

In Phase 2, Air Products pursued additional research efforts to further develop the VSA technology. Air Products also worked with Denbury Onshore to take the definitive project basis developed in Phase 1 and proceed through detailed design engineering and procurement (Sub-Phase 2A) and construction and commissioning (Sub-Phase 2B), culminating in ongoing operations (Sub-Phase 2C) in December 2012. The following sections provide more detail about the continued technology development and the specific activities associated with each of the sub-phases.

PHASE 2 TECHNOLOGY DEVELOPMENT

Early Project Phase Development of VSA Technology

Upon DOE's selection of the Port Arthur CO_2 capture project for Phase 2 funding, Air Products commenced with more advanced pilot-unit experiments of the VSA technology. The pilot unit was modified to allow a rinse step using an air-driven piston compressor with inlet and outlet surge tanks. An electric diaphragm vacuum pump was installed to generate the carbon dioxide product. In terms of adsorbent volume, the scale-up factor from this unit to a commercial system with 12'-diameter vessels is 27,000:1.

The development and design of commercial-scale adsorption systems was accomplished through a combination of cyclic lab-scale experiments and simulations of those experiments. Adsorbent characteristics were first determined through other lab-scale measurements. Pure component adsorption measurements were taken and fit to one of several available isotherm models, which were then used to predict the competition between different species for adsorption sites. Adsorption rate characteristic were derived from single-component breakthrough curves, providing parameters for mass transfer models. Pressure drop measurements were made in a column with flowing nitrogen. Once the relevent parameters were developed through independent laboratory measurments, the lab-scale pressure swing adsorption was simulated to verify models and parameters. The simulator-predicted scale-up from the one-inch diameter lab system to three- to twelve-foot diameter commercial systems has been verified through Air Products' experience with adsorption process design and operation.

Pilot-unit VSA experiments were conducted in June-July and September-October 2010 using a standard, readily-available CO_2-selective adsorbent. Following a change in operating conditions, the system reached cyclic steady state in ~3 hours. Most experiments were completed during working hours, with some extending overnight. The plot in Figure 12 summarizes the results and shows the tradeoff between product purity and carbon dioxide recovery. The lines connecting the individual points are representative of the carbon dioxide material balance error in each cyclic-steady state experiment. Within the reproducibility of the experiments, the tradeoff between product purity and carbon dioxide recovery is clearly established.

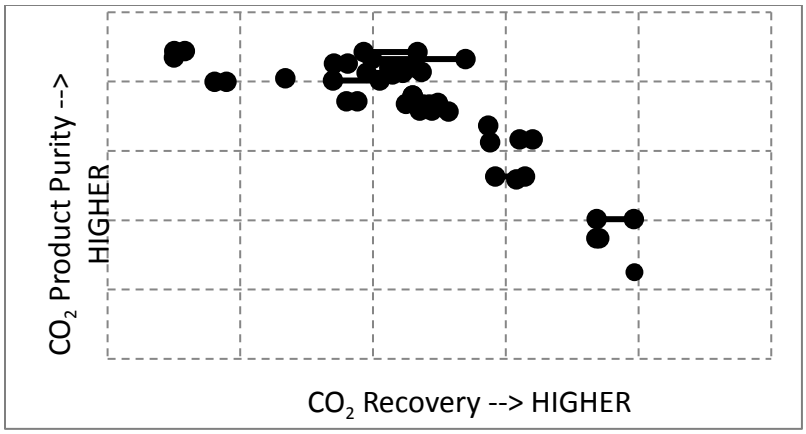

Figure 12. Relationship between CO_2 recovery and purity from VSA pilot-scale experiments.

In August 2010, measurements related to CO_2 VSA operation at Butler were made to assist with development of the VSA technology. The Butler VSA cycle was then run in the lab-scale VSA system to provide information on expected scale-up to commercial scale systems. Results from the operation at Butler and the pilot-unit VSA experiments were used to select parameters for the computer-based adsorption model. These parameters were adjusted until a reasonable match of all the relevant data was obtained. Final model parameters to support the Port Arthur project design were selected in late October 2010.

Development of Design Basis for Port Arthur

For the Port Arthur 2 feed gas conditions, computer model simulations were completed to understand the relationship between product purity, carbon dioxide recovery, adsorber size, and requirements for the vacuum and rinse flow on the commercial scale. Establishing these relationships enabled an efficient design for the Port Arthur CO_2 recovery process (adsorber vessel size, rinse compressor capacity, and vacuum blower capacity). After equipment sizing was complete, the adsorption process simulator was used to generate an expected operating curve. Figure 13 shows the expected tradeoff between the product purity and CO_2 recovery. From left to right, the curve shows the effect of running at shorter cycle times – less CO_2 is passed to the offgas stream and recovery increases, but product purity decreases because there is less sweeping of impurities from the column.

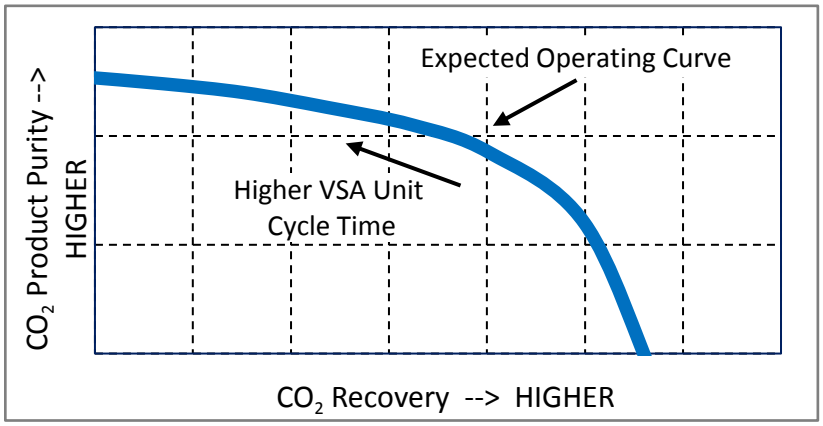

Figure 13. Expected operating performance curve for the Port Arthur VSA unit design.

SOLVING ENGINEERING ISSUES ASSOCIATED WITH DEPLOYMENT OF VSA TECHNOLOGY INTO AN SMR PROCESS

Deployment and integration of VSA technology into a SMR process presented several engineering challenges which needed to be solved during project execution. The following sections describe these challenges and how they were successfully resolved.

Existing Burner Operation with CO_2 Capture: Stability and Performance

Burner operation is vitally important to the reforming process in a SMR hydrogen plant, as the burners provide the heat required for the endothermic main reforming reaction. Flame characteristics such as shape, length, and temperature can impact heat transfer between the flue gas and process sides of the furnace. In addition to these factors, the flame must be stable across a broad range of operation, which is defined by the operating map of the overall facility.

In the original design of the Port Arthur plants, the main burner combustion fuel is the purge gas from the PSA unit. The purge gas has a high CO_2 content, which gives it a relatively high molecular weight and relatively low combustion energy (heating value). By implementing the CO_2 capture process upstream of the Port Arthur PSA units, the purge gas generated and used by the SMR burners is altered significantly. The volumetric flow of the purge gas is reduced, the heating value is increased, and the adiabatic flame temperature is increased. Each of these items can potentially change the flame characteristics. Through the course of the plant design, Air Products has evaluated the future performance of the burners to ensure they will function properly. A summary of the evaluations and outcomes are included in this report.

Single-Burner Stability Testing

A burner test is usually conducted when a significant process change is made to a facility that impacts a fuel stream. Because the changes to the purge gas for the CO_2 capture project qualify as a significant change, a complete burner test was conducted at the Callidus Technologies test facility in Beggs, Oklahoma. Callidus Technologies provided the original burners for both the Port Arthur 1 (PA1) and Port Arthur 2 (PA2) SMRs. The purpose of the test was to demonstrate that the existing burners could operate adequately with the new operating conditions imposed by the CO_2 capture project. A comprehensive test procedure was created to evaluate burner stability and performance for the following operating modes:

- Normal operation with CO_2-free purge gas and combustion air from Gas Turbine Exhaust (GTE) and Fresh Air Firing (FAF)
- Maximum rates with CO_2-free purge gas and combustion air from GTE and FAF
- Minimum rates with CO_2-free purge gas and combustion air from GTE and FAF
- Transitions cases with and without CO_2-free purge gas on both GTE and FAF
- Transitions from GTE to FAF with CO_2-free purge gas

Two burner designs are employed at each facility, with the main difference being that the outside rows of the reformer burner have a lower heat release since they provide heat only to a single row of reformer tubes. And while the PA1 and PA2 designs are similar, they are not identical – so these tests were performed on all four burner designs currently in use at the Port Arthur site. No stability issues were observed during the testing, and it was confirmed that the existing burner design would be adequate to handle the new operating conditions of the facility that incorporate the CO_2 capture process.

Furnace-Level Burner Stability

While a single-burner test provides much valuable information about the performance and operating map of the burners, it is unable to predict potential interactions between the burners that would result in poor performance in the field. To address this concern, a computation fluid dynamics (CFD) model was created to compare predicted furnace and burner operation with and without CO_2 capture. This model showed that while there are some slight differences in the flame shape and length, no flame impingement or flame interaction was predicted. It was concluded that the reformer would likely operate with comparable performance after the CO_2 capture facility was brought on-stream, and that no burner modifications would be required to maintain good combustion performance.

Fuel Distribution Study

It was understood that once the CO_2 capture facility went on-stream, the volumetric flow in the purge gas system would decrease. This would impact the operating pressure of the purge gas fuel header, which distributes gas evenly to the 100+ burners at each SMR. A study was conducted to evaluate if this change in pressure would have an impact on the purge gas distribution. CFD modeling was used to compare current operation of the fuel distribution system against future operation with the CO_2 capture facility on-stream. It was concluded that the changes in the fuel pressures would not have a significant impact on the fuel distribution to the burners.

Compositional Impacts – Burner Tip Corrosion

When CO_2 is removed from the purge gas, the resultant composition of the combusted flue gas also changes. Based on this change in composition, it was predicted that there would be an increase in the force driving metal dusting on the purge gas burner tips. Metal dusting is a form of corrosion that occurs under conditions where there is high carbon activity. To address the increased risk of metal dusting, new tips were installed on the Port Arthur SMR purge gas burners. These tips were treated so that the surface chemistry was modified by an aluminum alloy that will provide protection against metal dusting.

Summary and Results from Initial Operation

The outcome of the pre-operation testing lead to the conclusion that the existing burners were acceptable for the new purge gas composition, and no modifications are required that would affect flame stability. The only required burner modification related to the metallurgy of the purge gas burner tips and management of metal dusting. Replacement of the purge gas burner tips was completed prior to start-up of the CO_2 capture project. The stability and thermal performance of the burners at the Port Arthur SMR plants after the CO_2 capture plant was brought on-stream have met expectations.

Evacuation Blower Overpressure Protection

The broad operating pressure range required for the VSA technology creates a fundamental safety design issue to protect the evacuation blowers from being overpressured. The large size of the evacuation blowers, which are used to extract the product gas from the VSA adsorbers, makes it very difficult to design them for high pressure. Evacuation blowers of the required size are not common in the industry, and there is a limited number of suppliers who could meet the requirements for the Port Arthur project. Air Products evaluated two vendors to supply the evacuation blowers, and the design pressures they offered were <50 psig. Figure 14 shows the configuration of the evacuation blowers in the overall process scheme for the PA 1 and PA2 sites.

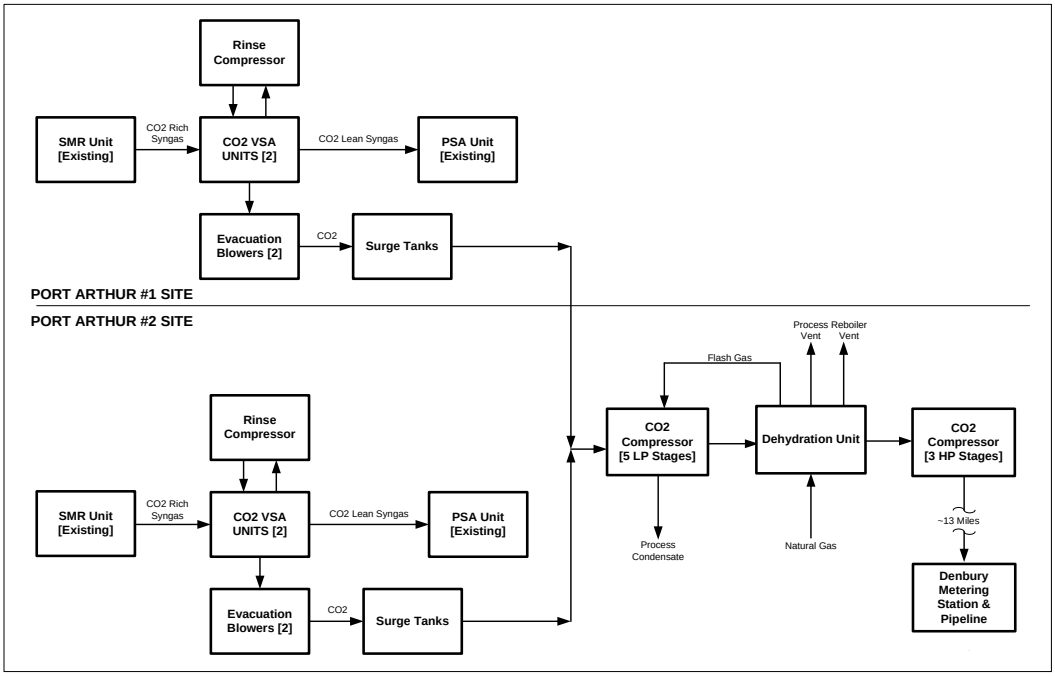

Figure 14. Basic process scheme for the Port Arthur CO_2 capture plant.

The specific cause of overpressure is an unintended or unanticipated opening of the evacuation valves which isolate the VSA adsorbers from the evacuation blowers. During the normal operating cycle of the VSA units, the adsorbers are usually at a pressure significantly above 50 psig. During this time, if the evacuation valves were to be opened for any reason, the high pressures in the VSA adsorber would rapidly pressure equalize with the evacuation blower. Due to the size of the VSA adsorber relative to the evacuation blower, this equalization would result in a pressure which would exceed the design pressure of the blower.

This type of overpressure scenario – failing open of a valve which separates a lower design pressure system from a high-pressure system – is a very common problem in the industry. Relief valves are typically used to safeguard against over pressurizing the lower design pressure system. In the case of overpressure of the Port Arthur evacuation blowers, the required relief flow demand makes it impractical to use of relief valves because of the large number of devices that would be required (over 75).

An alternate to relief valves are rupture disks, which are essentially thin plates designed to fail at a predictable pressure. Because they provide a much larger flow area, far fewer rupture disks would be required. However, rupture disks do not re-close after they are activated, have a tendency to prematurely fail, and can rapidly fail when exposed to a pressure which cycles (as with the Port Arthur VSA process). These characteristics create the potential for frequent shutdowns of the VSA unit to replace failed rupture disks.

Alternates to relief valves and rupture disks were developed and considered. These included the use of a water seal loop or a rupture pin valve in the evacuation header line leading to the blowers, which would rapidly close when high pressure is detected. Both of these alternate solutions were discarded when fundamental problems with them were identified.

Ultimately, over-pressurization concerns were addressed by using rupture disks with additional protective systems to decrease the frequency of both premature disk failure and opening due to an overpressure scenario.

SUMMARY OF SUB-PHASE 2A PROGRESS

PDC Facility and Air Products Pipeline Activity

Air Products' initial activity during Sub-Phase 2A was to establish and finalize the heat and material balance (H&MB) for the new plant and equipment associated with the PDC facility. Based on the finalized heat and material balance, key process specifications were issued to allow for the development of purchase parameters and requisition packages by Air Products' procurement group. The requisition packages were then issued for all major and critical path equipment, as well as for environmental consultants and select external engineering and design support.

The environmental consultant scope included the PDC Facility, as well as the lateral Pipeline and the Research MVA sub-projects. A Conflict of Interest form for the environmental consultant EA work was reviewed and approved by the DOE, and URS was selected as the environmental subcontractor.

As project work activities increased, additional project management resources were added, included an expert in Primavera to support the scheduling and reporting activities.

Based on the previously identified pipeline routing, title and survey work for the lateral pipeline was completed so that the pipeline environmental survey could be completed on schedule. Further, a kickoff meeting for all environmental work was held, attended by Air Products, DOE, and URS.

When the overall Front End Engineering and Design (FEED) for the PDC and Pipeline was completed, a kickoff meeting was held between Air Products and DOE senior management in Morgantown, WV. Subsequently, the Primavera Baseline Reporting Model was finalized.

With completion of FEED, Piping and Instrumentation Diagram (P&ID) Hazard and Operability (HAZOP) reviews were completed for the PDC and Pipeline.

Once an Environmental Questionnaire (EQ) was submitted and a Categorical Exclusion was subsequently approved by the DOE, all valves and materials for tie-ins (connection points) were ordered and the tie-ins were completed. The tie-ins were done during a scheduled site outage and allowed the existing system to be isolated from the new construction work; once the tie-ins were completed, subsequent work could be done without having to take the Port Arthur site out of operation. This was a critical schedule milestone as the initial tie-in activity needed to be coordinated with a previously scheduled site outage. A number of tie-in connections were made, including syngas from the existing SMRs, syngas back to the existing PSAs, cooling water, and nitrogen supply.

Packages were awarded to RDS Engineering for Outside Battery Limit (OSBL) engineering work and to Technip for detailed design activity.

MVA Activity

To facilitate the Research MVA Sub-Phase 2A work, electronic well logs, well spots and directional information for the West Hastings fault block B&C areas wells were provided to the UT BEG team.

Commercial Activity

During Sub-Phase 2A, commercial agreements were signed with external project participants. Finalizing these agreements was necessary to allow Air Products to move forward with the CO_2 Capture Project. The agreements are structured so that the CO_2 Capture Project can run beyond the DOE Demonstration Period.

The CO_2 supplied to Denbury Onshore is on a "take-if-tendered" basis up to 3,000 tons/day. The agreement Commencement Date was March 1, 2012, and there is no provision in the Denbury Agreement (except material default by Air Products) that allows Denbury Onshore to terminate the Agreement during the Demonstration Period.

A summary of progress at this stage of the project is included on the following pages for Sub-Phase 2A PDC Facility, Sub-Phase 2A Pipelines and Sub-Phase 2A MVA.

WORK PERFORMED AND RESULTS OBTAINED DURING SUB-PHASE 2A

PDC Facility - Project Management

For the PDC facility, Project Management included activities and/or materials required to plan and provide oversight for control and accounting throughout execution of Sub-Phase 2A. Project management encompassed a number of labor and material costs associated with the ongoing management of the project that are typically duration rather than schedule driven. A more specific description of these activities is provided in the following paragraphs.

During the Sub-Phase 2A period, primary Project Management reporting and scheduling activities included ongoing development of the Primavera reporting tool (PMP) and the monthly and quarterly reporting tools. The Primavera Baseline Schedule was finalized, and weekly Last Planner (Air Products' internal project management tool) sessions were held to monitor schedule.

In the environmental area, Project Management activities included development of an agreement with URS for environmental consulting services to support preparation of the Environmental Assessment (EA) package, organizing information requirements and scheduling for preparation of the EA and air permit application, and establishing a plan for testing the Port Arthur site for soils contamination and disposition.

Technical risks, some of which were included in the *Solving Engineering Issues Associated With Deployment of VSA Technology into an SMR Process* section, were identified, and recommendations for mitigation were developed. Similarly, key safety issues around the VSA / Blower operation were reviewed to allow finalization of the P&ID.

Project Management also worked with the procurement group to manage the front end of major equipment procurement, to develop package strategies for VSA vessel procurement and for execution of the tie-in work during the scheduled outage.

There were also significant Project Management external interfaces, including development of working agreement details for scope splits and organizing OSBL work, including the location of a project management resource at the site to coordinate design activities.

PDC Facility - Engineering

For the PDC facility, Engineering included activities performed by specific Air Products engineering leads for development of specifications, procurement packages, drawing reviews, technical supervision of vendors, and related activities throughout the execution of Sub-Phase 2A. Additionally, activities included those performed by consultants, third-party design firms and others in direct support of engineering activities required to design the PDC facility. A more specific description of these activities is provided in the following paragraphs.

A key early activity was the release and approval of the H&MB. Once that was completed, the Process Flow Diagram (PFD) was completed and Engineering released the process specifications and duties for long lead major equipment. P&IDs were developed, taken through Operability and Reliability Reviews, and then finalized.

Engineering also supported the further development of VSA technology with lab tests to provide design criteria for off-design conditions.

Support for the NEPA EA was provided as Engineering worked on documentation required for approval of the Environmental Contractor, developed preliminary process emissions data to support URS permitting activities. This included burner evaluation studies for the existing SMRs.

Working with Procurement, Engineering developed RFQs and evaluated proposals for critical equipment including the CO_2 Product Compressor, Product Blowers, Rinse Compressors, the Gas Turbine (GT) and the Heat Recovery Steam Generator (HRSG). Value improvement ideas were explored with major suppliers and specifications were revised accordingly.

Safety and reliability support was provided through evaluation of Blower allowable pressures and development of process specifications for VSA valves.

To support the schedule-critical ISBL tie-in work, Engineering issued RFQs for that work, evaluated bids, and completed the tie-in work in February 2011.

Engineering completed an electrical study to allow the across-the-line starting of the CO_2 compressor motor. Additional engineering and design information was provided to support various commercial agreements.

PDC Facility - Procurement

For the PDC Facility, this task included scheduling and accounting for all equipment and materials ordered by Air Products for the project and delivered to either the site or subvendors for field installation and assembly or prefabrication throughout the entire execution of the project. In addition to normal goods required for field construction, Procurement included contracts for: ‘turnkey’ supply of equipment; skid/ module fabrication; and area piping and steel fabrication. Each contract can require engineering, procurement, fabrication and/or testing to execute. A more specific description of these activities is provided in the following paragraphs.

As described above, Procurement released requisition packages for critical equipment including the CO_2 Compressor, GT, HRSG, Product Blowers and Rinse Compressors. Bids were reviewed and evaluated, scope was adjusted to optimized the split between shop work and field construction, and bid awards were made accordingly.

In addition, bid plans were developed and executed for VSA and Surge Tank Vessels, and valves, and Procurement also supported environmental permitting through development and award of a package to the environmental consultant.

Pipeline – Project Management

For the CO_2 pipeline lateral and hydrogen pipeline upgrade, Project Management included activities and / or materials required to plan and provide oversight for control and account through execution of Sub-Phase 2A. Project Management encompassed a number of labor and material costs associated with the ongoing management of the project that were duration rather than schedule driven.

To further develop the route, a centerline survey (conducted by ENI Global) was initiated after survey permission was obtained. Title searches were completed for the route, followed by easement acquisition.

Pipeline – Engineering

For the CO_2 pipeline lateral and hydrogen pipeline upgrade, Engineering included activities performed by specific Air Products engineering leads for development of specifications, procurement packages, drawing reviews, technical supervision of vendors, and related activities through the execution of Sub-Phase 2A. Additionally, activities include those performed by consultants, third-party design firms and others in direct support of engineering activities required to design the pipeline. The map and inset in Figure 15 show the location of the pipeline lateral relative to the Green Pipeline and the Port Arthur sites.

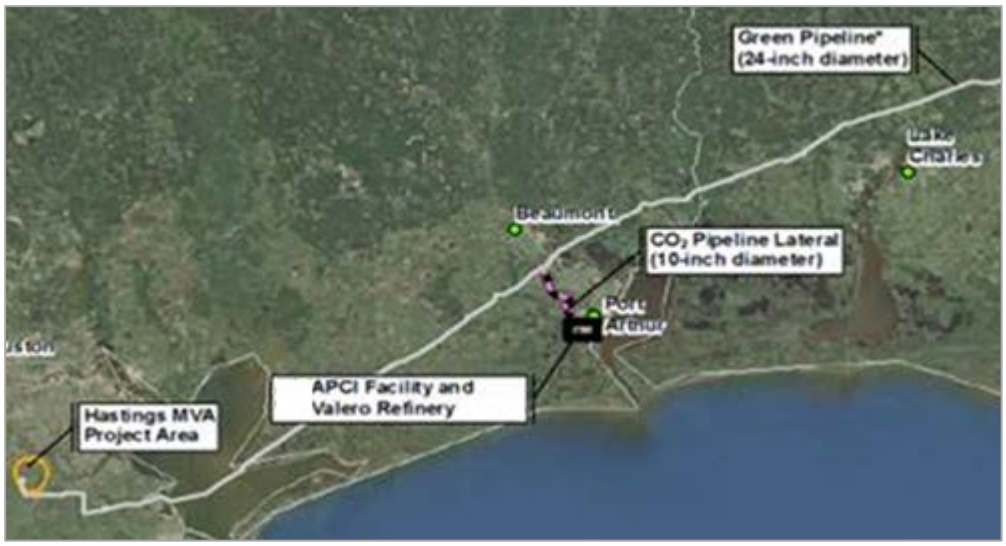

Figure 15. The Port Arthur facility, pipeline lateral and the Green Pipeline.

Engineering's specific activities during this phase included support of centerline survey, population survey and ductile fracture analysis, and work with URS on the EA/FONSI. Meetings were held with Texas Railroad Commission (TRCC) to discuss valve placement for water body crossings, and the Preliminary Flow Sheet was updated to reflect the actual pipeline design basis. Engineering also supported evaluation of various re-route options for several constrained areas of the original routing, modified the routing for a new tie-in point, prepared alignment sheets and supported preparation of a permit application with the city of Port Arthur. Several revisions were made to the Pipeline P&ID, and material take off quantities were developed to support procurement of construction materials. Horizontal direction drills (HDD) and detail sheets were also prepared in support of upcoming construction activities.

Pipeline – Procurement

For the CO_2 pipeline lateral and hydrogen pipeline upgrade, procurement activities include scheduling and accounting for all equipment and materials ordered by Air Products for the project and delivered to either the site or sub vendors for field installation and assembly or prefabrication throughout the entire execution of the project. In addition to normal goods required for field construction, Procurement included contracts for: 'turnkey' supply of equipment; skid/module fabrication; and area piping and steel fabrication. Contracts typically required engineering, procurement, fabrication and / or testing to execute. Procurement support was also needed for critical environmental permitting support and third-party supply of pipeline safety analysis.

Specific Procurement activities during Sub-Phase 2A included issuing a PO for environmental permitting support and support of the Environmental Assessment. Procurement also supported third party activities around biological and cultural surveys and title work for easement acquisition. An RFQ was issued for pipeline risk analysis with subsequent completion of that procurement.

In preparation for construction, Procurement issued a pipe order for bidding, and evaluated the resulting bids. The evaluation process included a mill visit in order to complete the appropriate due diligence for the selected vendor. Once the pipe order was placed, the bidding process began for valves and fittings. The pipe order was monitored to ensure the fabrication, coating and shipping was completed according to schedule. Small orders were then placed for materials needed later in the construction process, and Procurement negotiated POs to provide smart pigging of the future completed pipeline. Late-phase activity was focused on expediting various materials to support the construction schedule.

MVA – Project Management

For the Research MVA Activities, Denbury Onshore's project management activities included activities and/or materials required to plan and provide oversight for control and accounting through execution of Sub-Phase 2A. Project management encompassed a number of labor and material costs associated with the ongoing management of the Research project that are typically duration rather than schedule driven.

During the early part of this phase, project management activities included continued communications with the West Hastings Unit operational team for verification of field development and the initiation of negotiations for a subcontract between the University of Texas at Dallas (UTD) and Denbury Onshore for the modeling of 4D Gravity monitoring at Hastings Field, as well as negotiations for a subcontract with the University of Texas Bureau of Economic

Geology (UTBEG). Subcontracts were finalized in early 2011. During the Research MVA Activities, Denbury Onshore continued its normal enhanced recovery operations at the West Hastings Unit.

MVA – Engineering

For the Project MVA, Denbury Onshore's engineering activities included additional activities performed by specific Denbury engineering leads for development of specifications, procurement packages, drawing reviews, technical supervision of vendors and related activities throughout the execution of Sub-Phase 2A. Additionally, activities included those performed by consultants, third-party design firms and others in direct support of engineering activities required to conduct the Research MVA scope of the project.

During the early part of this phase, Denbury's engineering activities focused on the provision of data to the UT BEG team, including electronic well logs, well spots, and directional information for the Hastings fault block B&C areas wells.

Once contracts were finalized, kick-off meetings were held with UTD and UTBEG. UTD work during this phase focused on creation of a Gravity Model, while UTBEG tasks for Sub-Phase 2A included reservoir modeling / characterization, characterization of faults, soil gas feasibility test of surveillance, ground water monitoring, risk assessment and preparation of an updated Research MVA plan and cost distribution.

To support the work on these tasks, UTBEG made field visits during Sub-Phase 2A to collect soil gas and groundwater samples. A Sub-phase 2A interim report was submitted by UTBEG in September 2011.

Subsequent Sub-Phase 2A work by UTBEG included refining the static geologic model, ground water monitoring, and study of soil gas analysis. UTD used UTBEG's model and simulation results to plan surface and borehole gravity acquisition. Denbury Onshore's West Hastings Unit operational team identified four candidates for monitoring the Miocene completion interval and prepared detailed procedures which were sent to UTBEG for review.

MVA - Procurement

For the Research MVA Activities, Denbury Onshore procurement included scheduling and accounting for all equipment and materials ordered for the Research MVA Activities and delivered to either the site or sub vendors for field installation and assembly or pre-fabrication. In addition to normal goods required for field construction, Procurement participated in contract negotiations and administration with UTD, UTBEG and other vendors participating in the Research MVA project.

SUMMARY OF SUB-PHASE 2B PROGRESS

During Sub-Phase 2B, Air Products moved forward with full scale construction activities at the Port Arthur site. This activity was enabled by the DOE signature of the Finding of No Significant Impact (FONSI) and the approval of the facility air permits in July 2011. Initial construction activities focused on demolition of existing structures and site prep of the brownfield sites at PA1 and PA2. Foundation work and piling was completed during the winter of 2011-12, and equipment began arriving on-site in February 2012. Equipment was set and interconnecting piping and electrical work was completed over the summer of 2012, with the final piece of equipment, the

CO_2 compressor, being assembled in September 2012. Commissioning activities followed for PA2 with that unit in commercial operation in December 2012. Construction of PA1 was completed in early 2013, and that unit came on-stream in March 2013 when full CO_2 rates were supplied to Denbury Green Pipeline for delivery to the West Hastings EOR Project.

In parallel with the construction work at PA1 and PA2, construction of the Air Products CO_2 pipeline lateral was completed, as well as the required modifications to the hydrogen pipeline. Pipeline permitting was completed, all easements and right of ways were acquired (41 tracts), and construction began on 16 April 2012. Pipe construction (including HDDs) was completed in August 2012, followed by hydro testing, smart pigging, drying and cleaning. A cathodic protection system was also put in place. With the completion and commissioning of the Green Pipeline meter station, the Air Products CO_2 pipeline lateral was ready for operation in December 2012. During this period, a private pipeline operating and maintenance (O&M) agreement was completed with Denbury Green Pipeline as the O&M provider separate from the cooperative agreement.

For the Research MVA portion of the project sponsored by DOE, Sub-Phase 2B focused on continued data analysis, model development and preparation for ground water monitoring.

WORK PERFORMED AND RESULTS OBTAINED DURING SUB-PHASE 2B

PDC Facility – Project Management

In the initial stages of Sub-Phase 2B, Project Management oversaw the OSBL Piping and Electrical relocations as well as coordination of demolition and site prep. In parallel with that work, Project Management began coordinating ISBL detail design schedule with piling, civil, and other construction needs.

For the remainder of Sub-Phase 2B, Project Management's primary role was to develop construction packages for release and to support and oversee construction activities.

PDC Facility – Engineering

Engineering's initial activities in this phase focused on completion of piling and foundation design, and development of bid packages for various utility systems. Existing burner design was evaluated, and found acceptable provided certain metallurgy modifications were made. Remaining engineering activities were focused on support of construction and commissioning activities.

PDC Facility – Construction

The majority of Air Products' Sub-Phase2B activities were in the area of construction. Early work focused on site prep, including demolition of existing equipment and disposal of contaminated soil. Once that was completed, work began on piling and foundations as well as OSBL work for piping tie-ins and required power supply modifications. The two sites (PA1 and PA2) were generally worked in parallel, with PA2 activities just ahead of PA1 work. For example, once piling was completed at PA2, the pile rig was relocated to PA1 to begin piling work there.

Once piling and foundations were complete, setting of equipment began with the VSA vessels and skids first being put in place at PA2 and then at PA1. The setting of these skids was followed by the VSA blowers, surge tanks, and prefabricated piping and steel.

Cooling towers were then put in place, and work began at PA2 for erection of the HRSG. By June 2012, all foundation work had been completed at both sites, and assembly of the Gas Turbine Generator (GTG) had begun at PA2.

Setting of equipment and completion of interconnecting continued through the summer of 2012, with the CO_2 compressor assembly taking place in September of that year. Loop checking followed, and initial equipment runs were made in October 2012.

In November 2012, pressure testing was finalized for PA2 while adsorbent was loaded into the VSA vessels at PA1. Permanent power was supplied to PA2, and the cogen provided power during November. The CO_2 compressor was commissioned, allowing for HAZOP verification and the turnover of PA2 to Air Products' Operations team in December 2012

In January 2013, construction of PA1 continued with completion of the PA1 cooling tower system and electrical work. Construction of PA1 was completed in March, with full CO_2 rates being sent to Denbury Green Pipeline. Construction activities concluded with final site grading, paving, and fencing, as well as installation of insulation at both sites.

PDC Facility – Commissioning

Sub-Phase 2B Commissioning activities for the PDC began in September 2012 with commissioning of the PA2 cooling water system, line blows and degreasing for the cogen, line cleaning of the instrument air system and overall loop checking. In October, loop checking continued and utility systems (potable water, natural gas, steam, BFW) were commissioned. Cogen first fire happened in November, along with commissioning of the CO_2 compressor motor and the PA2 rinse compressor. In December, PA2 blower train run-ins were completed, the VSAs were saturated with CO_2 and the CO_2 compressor was started up. This completed the commissioning process for PA2.

PA1 commissioning followed a similar process, with commissioning of cooling water in January 2013, followed by blower train tests, rinse compressor commissioning and VSA saturation in February. PA1 commissioning was completed on 03 March 2013 with full CO_2 rates being supplied to Denbury via pipeline.

Overall, site commissioning went smoothly. A subsequent shutdown was planned for June 2013 to allow for correction of a vibration issue on the CO_2 compressor, and that shutdown was completed successfully.

Pipeline – Project Management

During the initial part of this phase, Project Management secured the permits required for the project, oversaw the ROW acquisition process for the pipeline lateral, and reviewed the contractor bids in preparation for actual pipeline construction. When construction began, project management oversaw those activities, moving on to the completion of the Green Pipeline meter station and the commissioning of the pipeline lateral.

Pipeline - Construction

Construction activities initiated with contact of landowners to advise them of construction schedules, coupled with staking, fencing and line location. Due to the nature of the routing geography, matting was put in place in wetland areas and bridges were placed over canals. Pipe was strung and placed in to excavated trenches. Welds were x-rayed to ensure weld integrity, and

a pipeline coating was applied. Certain areas require HDDs, with a total of 24 HDDs completed. Once the pipeline lateral was completed, the line was hydro tested and smart pigging took place. The line was then dried and cleaned; with the completion of the Green Pipeline meter station, the entire pipeline lateral was commissioned for use in December 2012.

MVA – Project Management

During Sub-Phase 2B, Denbury Onshore's project management team supported Engineering, Construction, and Commissioning activities.

MVA – Engineering

During Sub-Phase 2B, work by Denbury Onshore continued with Commercial Flood Monitoring Well Review and Remediation, developing maps, identifying wellbores in the MVA area, and initiating review of plugging records. Denbury Onshore engineering also supported research field work to prepare a monitor well in Fault Block C. Logging took place to further evaluate and profile the fault block.

Water samples were evaluated to obtain a broad understanding of the geochemistry in Hastings shallow aquifers, and soil gas sampling locations were chosen based on those results. Locations for soil gas sampling were chosen as well.

MVA – Construction

In the early part of Sub-Phase 2B, Construction activities included planning for various Above Zone Monitoring Interval (AZMI) wells and doing the well site preparation work for the May 2012 sidetrack of WHU-8409. This well drilled through the upper and lower Frio sands, allowing Repeat Formation Tests (RFT) pressures to be taken to determine the pressure profile across the Frio sands.

Other wells were sidetracked to provide additional monitoring points, and pressure readings were obtained to confirm containment of CO_2 within the target flood interval.

SUMMARY OF SUB-PHASE 2C PROGRESS

Sub-Phase 2C began in December 2012 with the commercial on-stream of the PA2 CO_2 capture facility. In March 2013, full commercial operation was achieved with the completion of the PA1 CO_2 capture facility.

Generally, Sub-Phase 2C went smoothly. A brief description of outages is as follows:

- An early outage was taken in June 2013 to modify the CO_2 compressor to eliminate a vibration issue.
- An outage was also taken in February 2014 for various reliability and performance enhancements.
- In October 2016, the CO_2 plants were shut down in conjunction with an SMR turn around. During this time, the CO_2 compressor was cleaned to recover capacity.
- In November 2017, an engine change out of the CO_2 cogeneration gas turbine generator was conducted. This was a scheduled change out that is in conjunction with the normal maintenance procedures for LM2500 gas turbine generators.

In summary, the operating performance has been very good, with outages typically needed only for normal maintenance activities.

In June 2014, the project hit a key milestone with the capture and sequestration of one million tons of carbon dioxide. Since then, the project has continued to perform consistently and achieved the four-million-ton milestone in October 2017.

For the Research MVA portion of the project, Sub-Phase 2C activities included well integrity logging utilizing soil gas and groundwater time-lapse surveillance, flood conformance vertical seismic profiles (VSP) and gravity time-lapse surveys, flood conformance real time bottom hole pressure (BHP) and logging time-lapse surveillance, and above-zone monitoring and fault monitoring.

WORK PERFORMED AND RESULTS OBTAINED DURING SUB-PHASE 2C

PDC – Management and Operations

During Sub-Phase 2C, PDC Management tasks focused on overseeing the ongoing operation of the PDC, with emphasis on 1) operator training and progression, and 2) specific activities to improve reliability and maintain safety performance.

Operating tasks focused on support of both day-to-day operation and the planned and unplanned outages. In addition to the ongoing operation, two key initiatives took place during Sub-Phase 2C:

1. The VSA systems were intentionally tripped to determine if the reliability safeguards were adequate to minimize the effect on hydrogen plant reliability
2. A CO_2 Capture Capacity Test was conducted to confirm that the capacity of the PDC was consistent with plant design.

A more through description of those initiatives is provided in the following pages.

Pipeline – Management and Operations

For the Pipeline, Sub-Phase 2C management tasks were accomplished through a field management structure that includes a pipeline foreman responsible for day-to-day compliance and safety of the facilities, a pipeline superintendent to whom the pipeline foreman reports and is accountable, and a regional manager to whom the entire pipeline and CO_2 group reports.

Pipeline Operations for Sub-Phase 2C included patrolling the pipeline facility by air, periodically inspecting the pipeline and conducing monthly calibrations of on-site electronic flow measurement equipment.

MVA – Management and Operations

During Sub-Phase 2C, Research MVA Management tasks include activities and material required to provide oversight and supervision of the MVA operations sponsored by DOE through execution of Sub-Phase 2C. Early phase work included the continuance of reservoir modeling, soil gas baseline surveillance, groundwater monitoring and monitoring the water injection rate in the Miocene. Conference calls and quarterly meetings were held with UTBEG to review soil gas and groundwater monitoring.

Operating tasks includes scheduling and accounting for all operating, maintenance, and utility costs associated with the actual Research MVA Activities throughout the execution of Task 2C. Early phase work included permanent seismic installations to establish a VSP baseline, and logging to generate the gravity baseline. Later, an injection profile was completed for Commercial Flood Monitoring, and a sensor test was carried out for soil gas monitoring. Groundwater level transducers were checked to confirm operation, and UTBEG performed a brine injection pulse test for analysis to update reservoir modeling.

Time-lapse seismic, time-lapse resistivity, and the time-lapse gravity operations were conducted the Q2 2013 through the Q4 2015. Seismic processing was completed in early 2016, and resistivity and gravity processing is ongoing.

In February 2015, a backup power source was added to all downhole pressure and temperature gauges to prevent data loss due to solar power. Three downhole Miocene monitor wells continue to monitor pressures, and two Frio pressure gauges in Fault Blocks B and C are also operational. A failure analysis of the three Schlumberger gauges installed in Frio wells determined a downhole short circuit of the gauge. Periodic bottomhole pressures are being conducted in Fault Blocks B and C to monitor reservoir pressure. Monitoring and analysis also continues throughout the phase for AZMI wells.

PHASE 2 SCHEDULE SUMMARY

Air Products' agreement with DOE commenced on 1 July 2010. Full notice to proceed with the project was received in March 2011. Planned on-stream for the first unit was 15 November 2012; actual on-stream date was 31 December 2012. The second unit was planned to be on-stream 1 January 2013; actual on-stream date was 6 March 2013.

MANAGING VSA SHUTDOWNS TO MINIMIZE IMPACT ON HYDROGEN SUPPLY

SMR Unit Transitions following Loss of VSA Trains

Implementation of the CO_2 capture process at the Port Arthur SMR plants introduces a new unit operation between the two main processing units used for hydrogen production – the SMR used to generate syngas, and the PSA unit used to produce pure hydrogen from the syngas. Furthermore, removing CO_2 from the syngas by the CO_2 capture VSA units appreciably impacts the operating characteristics of the PSA unit and SMR burners. A sudden loss (trip) of a VSA unit immediately impacts operation of the Port Arthur PSA unit and the SMR. If this transition is not successfully managed, any of the following negative outcomes could result:

- Hydrogen product purity could be lost, resulting in the need to stop supply of hydrogen to customers
- Excursions in SMR furnace operation could result in the need to:
  - Stop combustion of PSA purge gas, reducing syngas, hydrogen, and steam production
  - Stop feeding natural gas to the SMR, resulting in no hydrogen production and greatly-reduced stream production
  - Trip the reformer, resulting in little or no hydrogen production and risking the production of power from the gas turbine.

All of these potential outcomes are highly undesirable and could result in substantial impacts on the host refinery's operation, with the resultant loss of economic value. A plan and methodology was needed to manage VSA unit shutdowns to eliminate these negative impacts.

Air Products' approach to this engineering problem was three-fold:

- Identify and implement cost-effective design features to limit the frequency of VSA unit trips.
- Develop dynamic models of the trip event to identify effective control actions that could be applied to the operational transition to avoid the negative outcomes.
- Conduct live testing of the controlled response to a VSA unit trip during initial commissioning and start-up to validate the effectiveness of the control system.

Reducing the frequency of VSA unit trips was achieved by considering the causes of individual equipment or component failures that could result in VSA unit shutdown. Examples included failure of a switch valve to open or close at a prescribed time, loss of operation of one of the evacuation blowers, and an instrument reading failing to a trip condition. Failure events that would result in a VSA unit trip and which were considered likely to occur were addressed by developing cost-effective solutions. Examples of this include using switch valves for the VSA unit which had a proven track record (based upon Air Products' extensive experience with PSA units); using two-out-of-three voted instrumented trip logic, where failure of a single instrument could cause a trip; and conducting an extensive engineering review and test of the evacuation blowers before operation.

To manage and control the VSA trip transition, a two-part dynamic model of the process was developed. This included models of both the adsorption process and the steam methane reformer furnace. Once these dynamic models were linked together, they were evaluated for validity against available operating data. Use of the dynamic models involved an iterative process where a planned control response was defined and incorporated into the dynamic model of a given trip scenario. The model was then run and the results evaluated. The predicted response was analyzed to determine if it was acceptable, and, if not, what alterations to the planned controlled response were required. This process is shown in Figure 16.

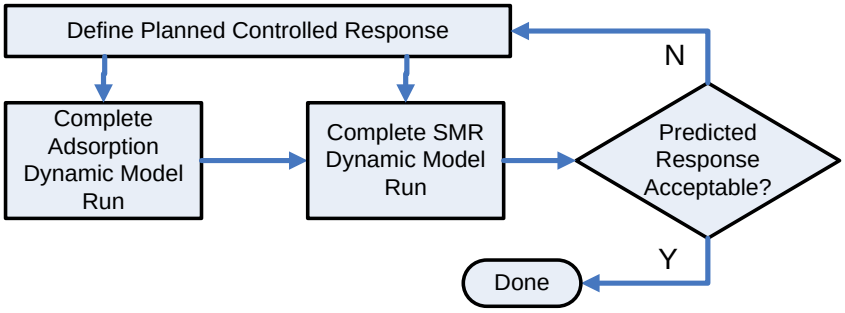

Figure 16. Logic diagram of Port Arthur dynamic simulation work for VSA unit trip response development.

Figure 17 depicts an example of the type of information developed by the dynamic model. It shows the response of the Port Arthur 2 SMR furnace excess O_2 as a function of time following a trip of one of the two VSA trains. If the excess O_2 reaches a zero value, there will be uncombusted

fuel in the furnace which could result in an uncontrolled energy release when this fuel eventually finds and combusts with available oxygen. To prevent this hazard, fuel supply to the Port Arthur SMRs is stopped when this condition is detected.

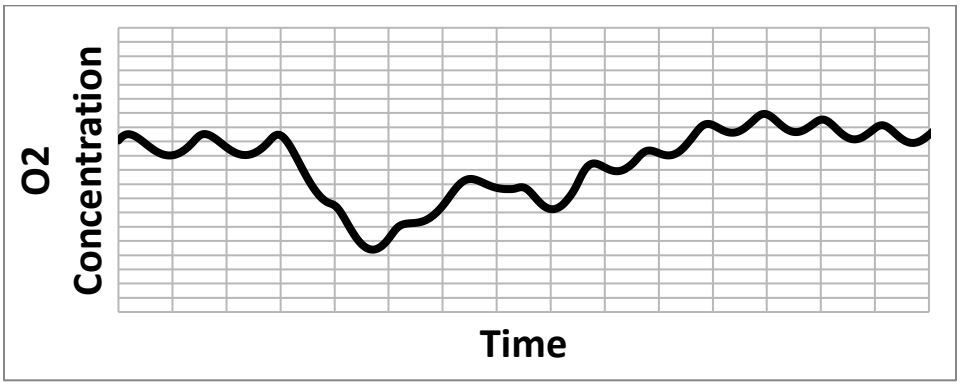

Figure 17. PA2 SMR excess O_2 response to a VSA train trip as predicted by dynamic modeling.

A trip of a VSA unit results in an oscillation of the excess O_2 because of the associated disturbance in PSA unit operation. If left uncontrolled, this oscillation could easily result in low excess O_2 and a trip of the reformer, with the associated loss of hydrogen production and steam. A planned, controlled response which limits the reduction in excess O_2 was developed based on information like this.

In all, eight different VSA unit trip conditions were evaluated using this method, four each for the PA1 and PA2 sites. The planned, controlled responses that were developed required modifications and additions to the existing control systems at both sites. This work was completed prior to bringing the VSA units online at both sites.

Immediately upon establishing operation of the VSA units at the Port Arthur 2 (December 2012) and Port Arthur 1 (March 2013) sites, tests of VSA trip conditions were conducted at each plant. Testing was conducted over the course of several days and incorporated tests with progressively greater impact. Results from these tests were compared to the results from the dynamic simulation work (Figure 18), and minor adjustments to the planned, controlled response were made as necessary.

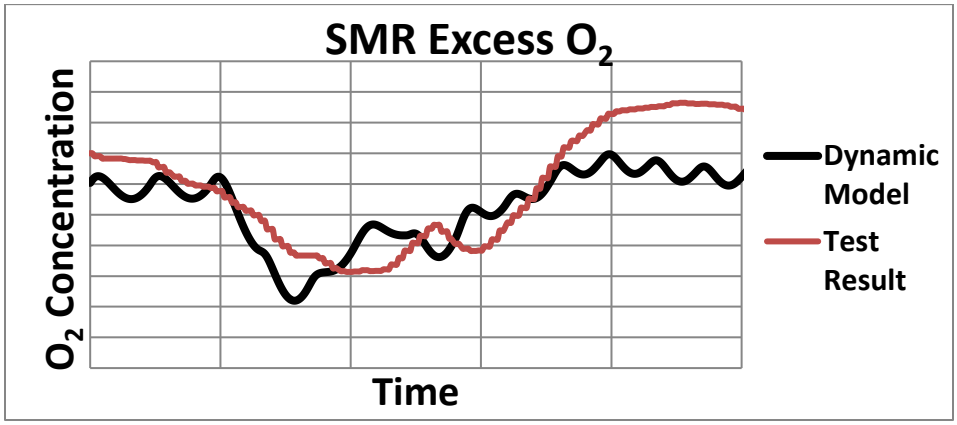

Figure 18. Comparison of results from plant testing of the dynamic model for a PA2 VSA trip.

The results from this testing largely corroborated the accuracy and usefulness of dynamic modeling. To date, all of the VSA unit trips experienced at the Port Arthur sites, whether purposely conducted as part of testing or due to an actual equipment or component failure, have been managed successfully without impacting the supply of hydrogen, steam or power to the plant's customers.

CO_2 CAPTURE CAPACITY TEST

PURPOSE

The main purpose of the CO_2 capacity test was to determine the amount of contained CO_2 that could be produced by the Port Arthur CO_2 capture plant and delivered to the transporter delivery station at the Green Pipeline tie-in point, enabling a comparison with the design production of 123.1 short tons/hr of CO_2. A secondary purpose was to establish the baseline plant performance to assist with future optimization, troubleshooting, and debottlenecking of the plant.

BACKGROUND

Overview of the Process

Air Products' Port Arthur steam methane reforming plants, known as Port Arthur 1 (PA1) and Port Arthur 2 (PA2), were commercially brought on stream in 2000 and 2006 respectively. PA1 produces hydrogen, power, and steam and is principally composed of a gas turbine which exhausts into a steam methane reformer (SMR). PA2 also produces hydrogen, power, and steam and is principally composed of a gas turbine which exhausts into both an SMR and a heat recovery steam generator (HRSG). Both plants utilize PSA units to generate a pure hydrogen stream from the syngas generated by the SMRs. The Figures 19 and 20 depict these basic process schemes.

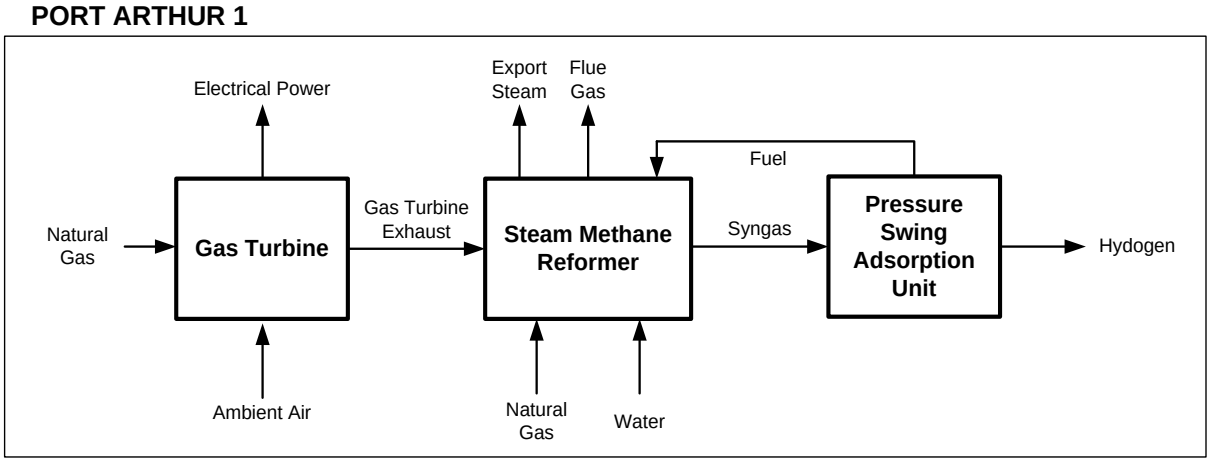

Figure 19. Port Arthur 1 basic process scheme (prior to CO_2 capture).

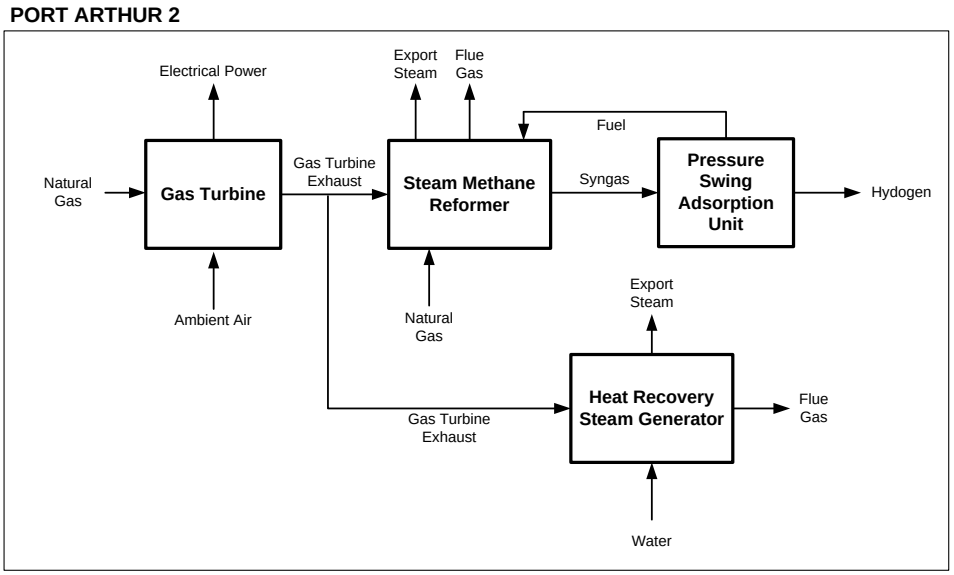

Figure 20. Port Arthur 2 basic process scheme (prior to CO_2 capture).

The CO_2 capture system at the Port Arthur plants uses a VSA process designed to remove >90% of the CO_2 contained in the syngas generated by the SMRs. This VSA process is upstream of the PSA units and consists of a set of adsorption vessels, evacuation blowers, a rinse compressor, and surge vessels. The CO_2-rich syngas from the SMR contains 10-20% CO_2, with the remainder of the stream being fuel (hydrogen and hydrocarbons) and inert gases. The CO_2 separated from the SMR syngas at each of the Port Arthur plants is combined prior to compression and drying for delivery to the Green Pipeline - Texas approximately 13 miles from the Port Arthur site. An illustration of the Port Arthur CO_2 capture system and how it is integrated onto the Port Arthur SMR plants can be found in the photographs in Figure 14.

Events Leading Up to the CO_2 Capacity Test

Table 2 provides a timeline of events related to operation of the CO_2 capture equipment at Port Arthur prior to the CO_2 capacity test.

Table 2. Summary of events leading up to the CO_2 capacity test.

Date	Description of Event
06-Dec-2012	First production of CO_2 from the PA2 CO_2 capture process
16-Dec-2012	First delivery of CO_2 to Denbury
16-Jan-2013	CO_2 capture process integration testing at PA2 completed
03-Mar-2013	First production of CO_2 from the PA1 CO_2 capture process
11-Mar-2013	Simultaneous operation of all CO_2 capture equipment first achieved
14-Mar-2013	CO_2 capture process integration testing at PA1 completed
14-18 April 2013	CO_2 plant total outage to complete project “punchlist” work
6-7 May 2013	CO_2 capacity test completed

PRE-TEST PREPARATIONS

Calibration of Instruments

An accurate test result is predicated on key process instrumentation functioning correctly and providing accurate data. Prior to conducting the test, all instrumentation related to performance of the CO_2 capture process was reviewed, and list of instruments and analyzers to be calibrated was developed. Except where noted, all of these calibrations were completed in the two weeks prior to the test.

In addition to the instrumentation at the Port Arthur site, the instruments at the metering and custody transfer station at the Green Pipeline - Texas tie-in point were calibrated on 17 April 2013. Denbury personnel calibrate instruments at this metering station on a monthly schedule and provide Air Products with a report following each calibration. As part of each calibration, Denbury updates the compositional basis for computing the density of the CO_2 measured by the station. During the CO_2 capacity test, the meter station was using the compositional basis listed in Table 3.

Table 3. Denbury metering station compositional basis during the CO_2 capacity test.

Component	Molar Concentration
Carbon dioxide	96.890%
Nitrogen	1.736%
Methane	0.605%
Carbon monoxide	0.163%
Hydrogen	0.606%

To calculate density, Denbury uses a commercially-available software package that replicates the NIST 14 thermodynamic database. This database has been widely accepted by the industry as a basis for estimating the density of supercritical CO_2 streams. It is important to note that the composition of the CO_2 being produced during the CO_2 capacity test was different than that listed in the Table 3. Therefore, a correction factor for the flow rate measured by this metering station must be applied to account for the compositional/density difference. This correction factor can be expressed at follows:

$$\text{Mass Flow Rate Correction Factor} = \text{sqrt}\left(\text{Density[Actual]} / \text{Density[Reference]}\right) \quad \text{Eq. 1}$$

Attainment of Test Conditions

To achieve maximum CO_2 production from the CO_2 capture plant, PA1 and PA2 must run at their maximum syngas generation capability, and all CO_2 capture equipment (four VSA/blower trains, two rinse compressors, and one CO_2 compressor/dryer system) must be in operation. As can be expected with most new facilities, early onset problems with equipment are experienced in the initial phases of operation. As recently as the day prior to the CO_2 capacity test, a problem with one of the four VSA/blower trains resulted in reduced CO_2 production over a short period of time (hours).

Production of syngas from the PA1 and PA2 SMRs is based on hydrogen production demand on Air Products H_2 pipeline system in the Gulf Coast. Although production demand from the H_2

pipeline system usually requires maximum production from the PA1 and PA2 SMRs, production issues at customer sites occasionally dictate that hydrogen production at the Port Arthur plants be curtailed. This decreases CO_2 production, since there is less CO_2 available in the syngas. Prevailing conditions of the Air Products Gulf Coast H_2 pipeline at the time of the CO_2 capacity test were such that H_2 production at the Port Arthur SMRs could be continuously maximized and did not impair the ability to maximize CO_2 production. Production from the PA2 SMR was maximized and brought to a steady production rate several days prior to the test. PA1 SMR production was maximized and bought to a steady production rate immediately prior to the test at approximately 8:00 am on 6 May 2013.

DESCRIPTION OF TEST AND DATA COLLECTED

After the PA1 and PA2 SMRs and all CO_2 capture plant equipment was brought to a maximum and steady-production condition, the CO_2 capacity test was considered to be commenced at 9:00 am CDT on 6 May 2013. It was run continuously for the next 24 hours, concluding at 9:00 am CDT on 7 May 2013. During this time frame, manipulation of the plant's operation was minimized to keep the plant at a steady operating condition.

Overall, the test was completed without any notable changes and was similar to what had been experienced in recent plant operation. Modest effects of ambient temperature on operation of the process and equipment were expected and observed. To counteract these effects, minor control adjustments were made to the operation of the CO_2 capture plant equipment. Hourly averages of CO_2 production, as measured by the Denbury metering station, varied from +1.7% to –1.8% during the 24-hour test period (Figure 21).

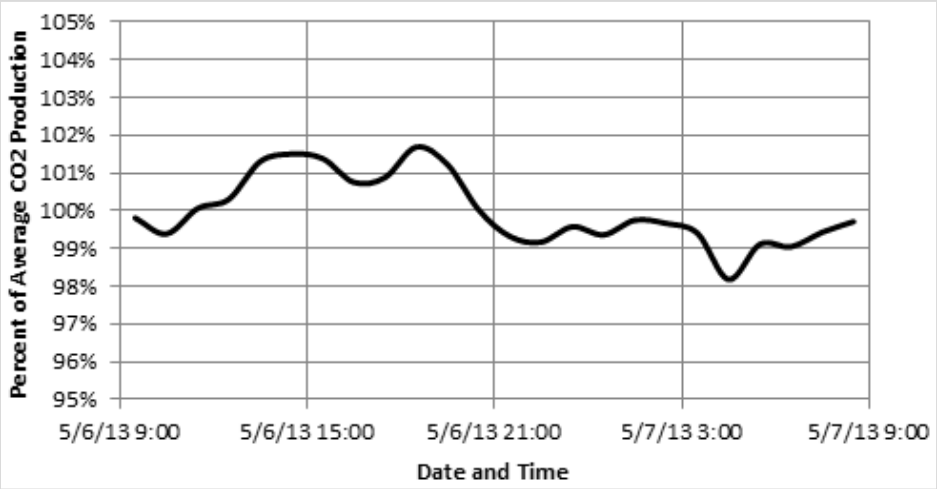

Figure 21. Variation in CO_2 production during the test.

The nominal purpose of the test was to demonstrate CO_2 capacity, and the metering station at the Green Pipeline - Texas delivery point provides this data. However, to validate the data from this metering station, a much broader set of data was collected during the CO_2 capacity test. This collection of data provides the basis for performing a reconciliation to identify errors in the data (i.e., instruments or analyzers which are reading incorrectly). This reconciliation can also build confidence in individual measurements by quantitatively showing consistency with other related data. The methodology used for this data reconciliation is described below in the Data Analysis and Reconciliation section.

In general, the data collected for the test was any available measurement related to performing a material balance for the PA1 and PA2 SMRs and the CO_2 capture plant. Table 4 summarizes the streams which define the overall material balance for the complete SMR and CO_2 capture plant process at Port Arthur.

Table 4. Streams which define a material balance of the CO_2 capture process.

Inlet Streams (11)	**Outlet Streams (9)**
PA1 SMR Natural Gas Feed	PA1 Process Condensate
PA1 Process Steam	PA1 PSA Product Hydrogen
PA1 Recycle Hydrogen	PA1 PSA Purge Gas
PA1 Blower N_2 Seal Gas Ingress	PA2 Process Condensate
PA1 VSA Unit Air Ingress	PA2 PSA Product Hydrogen
PA2 SMR Natural Gas Feed	PA2 PSA Purge Gas
PA2 Process Steam	CO_2 Product Compressor Condensate
PA2 Recycle Hydrogen	Dehydration Unit Vent Gas
PA2 Blower N_2 Seal Gas Ingress	CO_2 Product
PA2 VSA Unit Air Ingress	
CO_2 Compressor N_2 Seal Gas Ingress	

Data collected during the test fell into three general categories:

1. Data from the Port Arthur plant's regulatory control system. This comprised data from the PA1 and PA2 SMRs and the CO_2 capture plant.
2. Data from the Green Pipeline - Texas delivery point metering station. This data is transmitted from the metering station to the Air Products Port Arthur site via a data link.
3. High-pressure samples of the PA1 and PA2 natural gas feeds and the CO_2 product from the CO_2 capture plant. These samples were shipped to a lab for analysis.

Data in the first two categories was collected for every minute of the 24-hour test, and an average of this 1-minute data over 24 hours was calculated. This data was used for analysis. Data in the third category was from a limited number of samples (four each of the natural gas and product CO_2) and was primarily used to confirm the results from on-line analyzers that measured the same components. Generally, there was a high level of agreement between the results from the gas samples and the on-line analyzers.

DATA ANALYSIS AND RECONCILIATION

Data collected during the CO_2 capacity test are not necessarily correct or consistent (i.e., the data are not in perfect mass balance) due to measurement error. Data reconciliation is required to determine which data may be inaccurate and must be adjusted or disregarded to better represent performance. Any data reconciliation method is also not perfect and subject to error. However, if performed correctly, reconciliation improves upon the understanding of the data and overall plant and equipment performance. The methodology for the CO_2 capacity test was to apply the observed data to an overall material balance of the process and calculate the deviation of the observed data from the value which closes the material balance. A least-squares fitting of the data was performed according to the following equations:

$$\sum_{i=1}^{n} w(i) * e(i)\text{^}2 \quad \text{Eq. 2}$$

$$e(i) = [A(i) - D(i)] / M[i] \quad \text{Eq. 3}$$

where:

w(i) = a weighting factor, usually 1 for an included data point or 0 for an excluded data point
A(i) = the simulation data reconciliation value
D(i) = the data value being matched
M(i) = a scaling factor to align all the potential errors to the same order of magnitude
n = the number of data points being reconciled

A total of 44 data measurements was selected for the first pass of data reconciliation. Five data points were grossly inconsistent with the remaining data and thought to be incorrect, so they were not included in further analyses. The data reconciliation was repeated with the remaining 39 measurements, and an additional three data points were identified as most likely being incorrect. The final data reconciliation was performed with the remaining 36 of the 44 original data measurements. Results were excellent and showed a very high level of agreement and self-consistency. Specifically, there was an excellent matching of the flow rate measured at the Green Pipeline - Texas metering station (the data reconciliation value was only 0.3% different than the actual measured value). For comparative purposes, the design accuracy for this meter station is based on achieving a measured flow to within 1% of the actual flow.

RESULTS FROM THE TEST

The amount of CO_2 captured during the CO_2 capacity test was estimated in three different ways, as described in the following sections.

Raw Data from Denbury Green Pipeline Metering Station

The raw data from the Denbury Green Pipeline metering station is one basis for understanding the results of the CO_2 capacity test. This metering station data can be used to calculate the average amount of CO_2 contained in this stream. Table 5 summarizes the average metering station data for the 24-hour test.

Table 5. Data from the Denbury Green Pipeline metering station for the CO_2 capacity test.

Parameter	Units of Measure	Value
Mass Flow Rate	Mlbs/hr	258.6
Stream Composition:		
Carbon Dioxide	mol%	98.11%
Methane	mol%	1.08%
Hydrogen	mol%	0.16%
Carbon Monoxide	mol%	0.20%
Nitrogen	mol%	0.46%

The computation of the molecular weight of the stream is given in Table 6.

Table 6. Calculation of CO_2 product molecular weight.

Component	Component MW	Component Concentration [mol%]	Component Contribution to TOTAL MW
Carbon dioxide	44.01	98.11%	43.178
Methane	16.04	1.08%	0.173
Hydrogen	2.016	0.16%	0.003
Carbon monoxide	28.011	0.20%	0.056
Nitrogen	28.0134	0.46%	0.129
TOTAL			43.539

The resultant mass flow of contained CO_2 in the stream can then be calculated:

$$\text{Total Molar Flow of Stream} = \text{Mass Flow} / \text{MW} \quad \text{Eq. 4}$$

Total Molar Flow of Stream = 258,600 lbs/hr / 43.539 lb/lbmol
Total Molar Flow of Stream = 5,939.5 lbmol/hr

$$\text{Molar Flow of } CO_2 \text{ in Stream} = \text{Total Molar Flow of Stream} * \text{Molar Conc. of } CO_2 \quad \text{Eq. 5}$$

Molar Flow of CO_2 in Stream = 5,939.5 lbmol/hr * 98.11%
Molar Flow of CO_2 in Stream = 5,827.2 lbmol/hr

$$\text{Mass Flow of } CO_2 \text{ in Stream} = \text{Molar Flow of } CO_2 \text{ in Stream} * CO_2 \text{ MW} \quad \text{Eq. 6}$$

Mass Flow of CO_2 in Stream = 5,827.2 lbmol/hr * 44.01 lb/lbmol
Mass Flow of CO_2 in Stream = 256,500 lb/hr (= 128.3 short tons/hr)

Denbury Green Pipeline Metering Station – Corrected Density

As described above, the Denbury Green Pipeline metering station does not continuously update the compositional basis of the stream being measured. This introduces error in the measurement because the actual density of the stream flowing across the meter is different than the reference density of the stream programmed into the meter based on previous data. A correction factor to remove this error can be computed by calculating stream densities the based on the composition of both the reference and actual stream conditions. Table 7 shows the reference composition and density and the actual composition and density for the CO_2 capacity test.

Table 7. Reference and actual composition and density of CO_2 product.

Parameter	Units of Measure	Reference Condition	Actual Test Condition
Pressure	psia	1920	1920
Temperature	°F	76.21	76.21
Density (Note 1)	lb/ft^3	51.118	51.881
Stream composition:			
Carbon dioxide	mol%	96.89%	98.11%
Methane	mol%	0.605%	1.08%
Hydrogen	mol%	0.606%	0.16%
Carbon monoxide	mol%	0.163%	0.20%
Nitrogen	mol%	1.736%	0.46%

Note 1 – Density Correction Calculations:

Based on this information, the correction factor for the Denbury Green Pipeline meter station results is:

Mass Flow Rate Correction Factor = sqrt (Density[Actual] / Density[Reference]) Eq. 1

Flow Correction Factor = sqrt (51.881 / 51.118)
Flow Correction Factor = 1.0074

The density-corrected Denbury Green Pipeline meter station flow measurement is then:

Denbury Green Pipeline Meter Station Flow (Density Corrected) =
Flow Correction Factor * Denbury Meter Station Flow (Raw Data) Eq. 7

Denbury Green Pipeline Meter Station Flow (Density Corrected) = 1.0074 * 258.6 Mlbs/hr
Denbury Green Pipeline Meter Station Flow (Density Corrected) = 260.5 Mlbs/hr

The contained CO_2 flow can then be computed in a similar manner as in the previous section.

Total Molar Flow of Stream = Mass Flow / MW Eq. 4

Total Molar Flow of Stream = 260,500 lbs/hr / 43.539 lb/lbmol
Total Molar Flow of Stream = 5,983.7 lbmol/hr

Molar Flow of CO_2 in Stream =
Total Molar Flow of Stream * Molar Concentration of CO_2 Eq. 5

Molar Flow of CO_2 in Stream = 5,983.7 lbmol/hr * 98.11%
Molar Flow of CO_2 in Stream = 5,870.6 lbmol/hr

Mass Flow of CO_2 in Stream = Molar Flow of CO_2 in Stream * CO_2 MW Eq. 6

Mass Flow of CO_2 in Stream = 5,870.6 lbmol/hr * 44.01 lb/lbmol
Mass Flow of CO_2 in Stream = 258,400 lb/hr (=129.2 short tons/hr)

Contained CO_2 Flow Rate from Data Reconciliation

One additional estimate of the contained CO_2 achieved during the capacity test comes from the data reconciliation. This result was 128.6 short tons per hour.

Summary of Results and Expected Confidence Level

Table 8 summarizes the estimations of contained CO_2 measured or calculated during the CO_2 capacity test conducted on May 6-7 at the Port Arthur CO_2 capture plant. These figures are compared with the values used to design the plant ("CO_2 Plant Design Basis").

Table 8. Summary of results from the CO_2 capacity test.

Basis	**Contained CO_2 Product** [short tons per hour]	**% of Design**
CO_2 Plant Design Basis	123.1	100.0%
Denbury Green Pipeline Meter Station – Raw Data	128.3	104.2%
Denbury Green Pipeline Meter – Corrected Density	129.2	105.0%
Data Reconciliation	128.6	104.5%

As be seen in Table 8, all three methods used to estimate of the amount of CO_2 captured during the CO_2 capacity test exceed the original design basis amount by several percentage points. Additionally, the narrow range of these three estimates, from 104.2% to 105.0% of the design basis, implies a high level of confidence in these results and indicates that the Denbury Green Pipeline metering station is providing an accurate measurement of the amount of CO_2 captured.

OVERALL CONCLUSIONS, CURRENT STATUS AND INDICATIVE ECONOMICS

The demonstration project has performed well, coming on-stream in accordance with the planned schedule and operating with few unscheduled outages. On-stream since December of 2012, the project has met the stated goals, consistently capturing and sequestering CO_2 at a rate of approximately one million tons per year. A "lessons learned" session was held with the Department of Energy in 2016 to provide an overall summary of the project performance. An overview of that information is as follows:

- The adsorption technology development and scale up was flagged as an initial technical challenge which the team was able to overcome within the planned project timeline.
- Reliability of the existing hydrogen facilities was not impacted due to a high level of operational planning and testing.
- Project success was facilitated by the Gulf Coast location, allowing Air Products and Denbury to leverage existing resources and infrastructure there.
- While the Gulf Coast location provided resources and infrastructure, the installation of a new project of this scale at an existing operational site required additional planning and execution resources to ensure the existing Plant operations were not impacted.
- The project would not have been successful without the cooperation and facilitation of several project participants, including Denbury Onshore.

With respect to current status, the project continues to operate well, with no major maintenance expected beyond normal preventative maintenance activities. The DOE demonstration period concluded in September 2017, and current plans are to remain in operation for at least the next few years.

INDICATIVE ECONOMICS

This project would not have been economically feasible without the funding provided by the Department of Energy. Table 9 shows the indicative economics in US dollars per metric ton for this project, excluding that Department of Energy funding benefit.

Table 9. Indicative economics for the Port Arthur project. All calculations assume a CO_2 production level of 1,000,000 metric tons per year

Cost Category	USD/Metric Ton	Comments
Installed Capital Cost	$51.00	See Note 2
Natural Gas	$5.10	See Note 3
Miscellaneous Utilities	$0.90	
Property Tax	$5.00	
Labor and Maintenance	$4.50	See Note 4
Gross Total Cost	$66.50	See Note 5
Net Total Cost	$76.50	See Note 6

Notes:

1. All calculations assume a CO_2 production level of 1,000,000 metric tons per year.

2. Installed Capital Cost was approximately $300,000,000; this includes CO_2 capture equipment, the CO_2 pipeline to connect Port Arthur with Denbury Green Pipeline, the CO_2 compressor and the cogeneration unit. Calculation assumes an annual capital recovery factor of 0.17, based on a 15-year life and a 10% return on capital.

3. Natural Gas includes natural gas utilized by the cogeneration unit as well as efficiency impacts on the existing hydrogen plants. This assumes natural gas pricing of $3/MMBTU.

4. Labor and maintenance costs are incremental to those costs associated with pre-existing operations at the Port Arthur site.

5. Economics shown do not include any costs associated with Monitoring, Verification and Accounting (MVA) of sequestered CO_2 and exclude the effect of a new CO_2 source as a result of the energy used to capture the CO_2.

6. Economics shown do not include any costs associated with Monitoring, Verification and Accounting (MVA) of sequestered CO_2 and include the effect of a new CO_2 source as a result of the energy used to capture the CO_2.

APPENDIX: ACRONYMS AND ABBREVIATIONS

AZMI	above zone monitoring interval
BHP	bottom hole pressure
BMP	best management practice
CFD	computational fluid dynamics
COGEN	co-generation system
CCS	carbon capture and sequestration
DEA	diethylamine
DGA	di-ethylene glycolamine
EA	environmental assessment
EIV	environmental information volume
EOR	enhanced oil recovery
EQ	environmental questionnaire
FAF	fresh air firing
FEED	front end engineering and design
FONSI	findings of no significant impact
GTG	gas turbine generator
GTE	gas turbine exhaust
H&MB	heat and material balance
HAZOP	hazard and operability
HDD	horizontal direction drills
HHV	higher heating value
HRSG	heat recovery steam generator
ISBL	inside battery limit
MDEA	methyl-diethanolamine (aMDEA = activated MDEA)
MEA	monoethylamine
MM	million
MMSCFD	million standard cubic feet per day
MVA	monitoring, verification and accounting
MW	megawatt
O&M	operation and maintenance
OSBL	outside battery limit
P&ID	piping & instrumentation diagram
PDC	purification, dehydration and compression
PFD	process flow diagram
PMP	Primavera reporting tool
PSA	pressure swing adsorption
PTSA	pressure variation during temperature swing adsorption
RFT	repeat formation tests

ROW	right of way
SCFD	standard cubic feet per day
SCR	selective catalytic reduction
SMR	steam methane reforming
TEG	triethylene glycol
TSA	temperature swing adsorption
TPY	tons per year
UTBEG	University of Texas Bureau of Economic Geology
UTD	University of Texas at Dallas
VPSA	vacuum swing adsorption below atmospheric pressure
VSA	vacuum swing adsorption
VSP	vertical seismic profile
WGC	West Gulf Coast
ZLC	zero-length chromatography