

Air Products Pressure Swing Adsorption at the National Carbon Capture Center

Project Objectives

Gasification is a promising alternative to traditional coal-fired combustion that can be adapted to CO₂ capture while supplying synthesis gas (syngas) for hydrogen, power, or chemical products. A key challenge for coal gasification is to reduce its cost. Downstream processing of syngas for CO₂ capture requires separation of the crude stream into the desired products (H₂/CO), a sulfur stream (primarily H₂S), and sequestration-ready CO₂. The process most commonly employed for this separation is acid gas removal (AGR) based on absorption in a physical solvent. Air Products has developed a proprietary alternative that consists of two process blocks: Sour Pressure Swing Adsorption (PSA) that separates CO₂ and H₂S from the desired products, and a tailgas disposition block which separates the sulfur-containing compounds and purifies the CO₂ to a sequestration-grade product (see Figure 1). Sour PSA is the key enabler of the technology, but only limited testing of the adsorbent technology has been performed on high-hydrogen syngas streams.

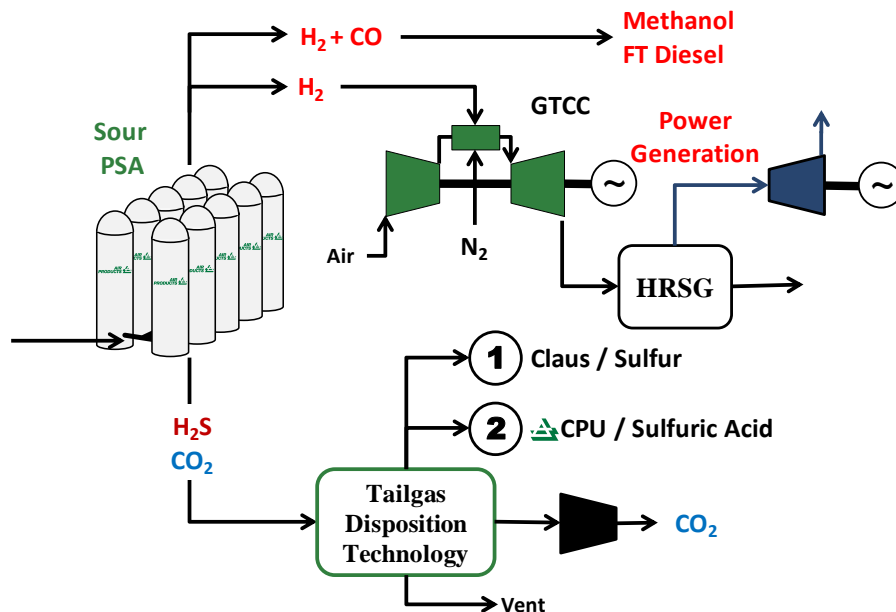


Figure 1. Sour PSA System

Air Products successfully demonstrated under DOE project DE-FE0007759ⁱ a 4% reduction in cost of electricity (COE) from a low-rank coal-based, integrated gasification and combined cycle (IGCC) plant with CO₂ capture. This represents a 14% decrease in the cost of carbon capture compared to the NETL S3B reference caseⁱⁱ. However, testing to date was only conducted for one week periods of time and did not allow for prolonged stability testing on authentic syngas. This is a critical limitation for commercialization that will be addressed in our proposal.

In this project, Air Products proposes to operate a two-bed mobile system at the National Carbon Capture Center (NCCC) facility. A slipstream of authentic, high-hydrogen syngas based on low-rank coal will be evaluated as the feedstock. Testing will be conducted for approximately eight weeks, thereby providing far longer adsorbent exposure data than demonstrated to date. By utilizing real-world, high-hydrogen syngas, information necessary to understand the utility of the system for methanol production will be made available.

In addition, Air Products will also operate a multi-bed PSA process development unit (PDU), located at its Trexlertown, PA headquarters, to evaluate the impact of incorporating pressure equalization steps in the process cycle. This testing will be conducted utilizing a sulfur-free, synthetic syngas, and will improve the reliability of the prediction of the system's operating performance at commercial scale.

Finally, information obtained from both the two-bed PSA system operated with authentic high-hydrogen syngas and the multi-bed system operated with synthetic syngas will be combined to build a techno-economic analysis (TEA) of Sour PSA utilization for methanol production. It will also be used to update the TEA already completed for IGCC in the above-referenced DOE project.

ⁱ. *Advanced Acid Gas Separation Technology for the Utilization of Low Rank Coals*, DE-FE0007759, Dec. 2012

ⁱⁱ. Black, J.B. *"The Cost and Performance Baseline for Fossil Energy Plants - Volume 3A: Low Rank Coal to Electricity: IGCC Cases,"* DOE/NETL, 2010/1399

Background

The major benefit of Sour PSA discovered in the techno-economic studies conducted to date is the reduction in capital cost of the acid gas removal system. Estimates from studies on H₂ production for refinery applications and clean power indicate a projected savings of >14% in capital cost for purifying the syngas and producing CO₂ and sulfur products. This leads to a significant reduction in the cost of CO₂ capture. Based on CO₂ capture case studies conducted to date, Sour PSA technology and Rectisol[®] and Selexol[™] technologies are about the same on an operating cost basis. When producing power from a high-sulfur fuel, up to an estimated 4.5% of additional net power is produced from the plant.^{ii,ii} The results are sensitive to the feedstocks and gasification technology employed. Recent experimental validation of the models used to predict the benefits of a large-scale, commercial plant was key to increasing confidence in the results of the studies. A long-term study of Sour PSA performance on gasified low-rank coal is essential to provide a more robust assessment of the system's long-term performance and economic benefits when applied to syngas plants. A comparison of state-of-the-art acid gas removal technologies and the Sour PSA system is presented in Table 1.

Table 1: Comparison of Technologies for CO₂ Capture from Gasification Systems

Capability	Conventional Technologies - (physical solvent absorption process such as Selexol™ or Rectisol®)	Air Products' Advanced CO₂ Capture System
Applicable end markets (Clean Power/Syngas/H ₂)	Power, syngas or H ₂ (with some limitations) or combinations thereof	Power, syngas, H ₂ or Poly-gen
Produce product gas at pressure	Yes	Yes
Ability to produce high- purity H ₂	No, needs another unit operation (PSA). Needs a sink for low BTU PSA tail gas.	Yes
Ability to produce high- quality syngas	Good; but limitation on purity from non-acid gas impurities; N ₂ , Ar, CH ₄ , etc., slip to product	Better; non-acid gas impurities like N ₂ , Ar, CH ₄ removed by PSA
Availability of high- quality heat	Single location-sour syngas cooling system	Multiple locations - both oxy- combustion system and sour syngas cooling system
Capital expense	Significant portion of power plant scope	Reduced portion of power plant scope
Operating expense	Solvent costs and power costs (especially for refrigeration). CO ₂ compression power.	Incremental O ₂ for combustion. CO ₂ compression power.
Economies of scale	Economic only at large scale	Economic at small and large scale
Carryover of contaminants to syngas	Yes, solvent losses to product gas	No, application of solid sorbent in a fixed bed
Claus plant required	Yes	No, optional
Sulfur export form	H ₂ S (for later processing)	H ₂ SO ₄ or H ₂ S (for later processing)
Amenable for CO ₂ capture	Yes, with design changes	Yes
Ability to retrofit for CO ₂ capture	Yes, but may require major modifications	Yes, capture grade available without major modifications
% CO ₂ capture	~90% max; > 90% requires more extensive integration, unit operation, and capital and operating expense	>95%

A. OBJECTIVES

In this project, Air Products proposes to operate a two-bed mobile pressure swing adsorption (PSA) unit at the National Carbon Capture Center (NCCC) facility utilizing a slipstream of authentic, high-hydrogen syngas generated from low-rank coal. Testing will be conducted for approximately eight weeks, therefore providing data on a far longer adsorbent exposure period than has been demonstrated to date. By utilizing high-hydrogen syngas, it will provide information necessary to further understand the utility of the system for methanol production. Air Products will also operate a multi-bed PSA process development unit (PDU), located at its Trexlertown, PA headquarters, to evaluate the incorporation of pressure equalization steps in the PSA cycle, and to improve predictions of system operation at commercial scale. This testing will be conducted utilizing a sulfur-free, synthetic syngas. Lastly, information obtained from the PSA system operated with authentic high-hydrogen syngas and the multi-bed system operated with synthetic syngas will be combined to 1) build a techno-economic assessment (TEA) of PSA utilization for methanol production; and 2) update the existing TEA for IGCC provided in DOE project DE-FE0007759. The entire project will be conducted in one budget period. The objective of Task 1 is to manage the project efficiently and cost-effectively. The objectives of Task 2 are to construct a weatherproof, mobile system containing a guard bed unit in series with a pre-existing Sour PSA unit, and to install the mobile system in a suitable location at the NCCC facility in Wilsonville, AL. In Task 3, the objective is to evaluate PSA performance with authentic syngas containing high levels of CO and H₂ in prolonged testing for approximately eight weeks. The objective of Task 4 is to operate a multi-bed PSA incorporating pressure equalization steps, utilizing a sulfur-free, synthetic syngas. The objectives of Task 5 are to perform a TEA based on the experimental data to predict the economic benefits of incorporating Sour PSA for chemicals production from low-rank coal, as well as to update the TEA for the already-conducted IGCC case.

Task 3.0 – Operate TSA and PSA Unit and Evaluate Performance

Subtask 3.1. Operate the TSA/PSA Module. After connecting them to the NCCC system (Task 2), Air

Products shall pack the guard bed and PSA vessels with fresh adsorbent. Air Products shall conduct a series of CO and H₂S breakthrough tests with the PSA to determine the initial adsorption capacities. The mobile system will then be operated in cyclic mode with pressurized sour syngas from NCCC's gasifier (taken after gas cooling and knockout of condensable species by NCCC). Air Products, or NCCC with Air Products' guidance, will run the PSA in cyclic mode with sour feed gas for a total on-stream time of approximately eight weeks. The PSA operator will modify the feed gas rate to maintain a desired level of H₂S in the PSA product gas. Air Products will then assess PSA stability and performance by evaluating the CO₂ and H₂S rejection and the CO and H₂ recovery to the product gas. The breakthrough of benzene from the guard bed unit shall be monitored by gas chromatography (GC) to determine relative performance during the test period. NCCC or Air Products shall periodically withdraw gas samples to characterize the levels of H₂, CO, CO₂, H₂S, and N₂ in the feed, waste, and product gas streams. After consultation with NCCC to determine the most effective approach, Air Products or NCCC shall determine the fate of trace-level contaminants. At the end of the testing period, Air Products shall conduct a second set of CO and H₂S breakthrough experiments to determine if the adsorption characteristics of the PSA have changed with exposure. Air Products will remove the guard bed and PSA adsorbent beds and ship them to Trexlertown for sample extraction and post-mortem studies of the adsorbent.

Subtask 3.2. Conduct Post-Mortem Analysis. Air Products shall conduct lab tests, including thermogravimetric analysis (TGA), surface area analysis and chemical composition, to evaluate the relative condition of the exposed adsorbents. Air Products will conduct SIMPAC process simulations at the experimental conditions of the Sour PSA tests and compare the results with the observed performance. SIMPAC has been previously developed at private expense, and shall be considered as Restricted Computer Software for the purposes of this project.

Test Unit Description

The test unit consisted of a pretreatment skid followed by a PSA skid. The pretreatment skid contained

a two-bed guard bed used to remove organic tar species from the raw syngas, an electrically classified compressor for compression of the clean sour syngas to ~350 psig, and an air cooled cooler/knockout assembly for rejecting water and other condensables from the sour syngas. This gas was then passed to the sour PSA skid where it entered one of two PSA vessels containing adsorbent for the removal of sulfur species and CO₂. The cleaned gas exiting the PSA was characterized (flow, composition) and vented to the NCCC thermal oxidizer. Each bed was cycled through the predetermined PSA cycle steps. During the regeneration steps the bed was depressurized, purged with product gas at atmospheric pressure, and then re-pressurized with product gas. Gas exiting the bed during regeneration was also characterized and vented to the thermal oxidizer. The PSA product gas composition was monitored during cycling. Once stable, the inlet and outlet gas flows / compositions and column pressure/temperatures were measured during one cycle to provide data for comparing with process simulations.

Summary of Campaign

A set of CH₄ and H₂S breakthrough tests were conducted on each of the PSA beds before syngas was introduced to the unit. The fresh adsorbent capacities were in line with the expected values from previous isotherm measurements.

Feed of sour syngas to the system was started on 10/8/2014 at 10AM. The sour syngas passed through the guard beds where organic tars were adsorbed. We monitored progression of the tars through the bed by measuring the benzene level in the inlet and outlet syngas. The inlet level was typically around 300 ppm (molar basis) and no evidence of benzene was ever detected in the guard bed effluent gas. The guard bed does a great job of eliminating tar species from the syngas stream. H₂S is also removed from the gas by this adsorbent. Our previous experience at the Energy and Environmental Research Center suggested that breakthrough of H₂S from the guard beds would take about 2-5 days. Instead, in part due to the much lower H₂S level in the feed gas (~300 ppm compared to 2400 ppm), the breakthrough time was much longer. After 8 days on sour syngas, we decided to accelerate the breakthrough of H₂S by feeding 0.5% H₂S/He cylinder gas to the unit at atmospheric pressure, thereby loading the adsorbent with

H2S more rapidly than via the sour syngas. This approach was successful and sour syngas started to pass through the guard bed on 10/21. The PSA was then started on the sour syngas feed.

The PSA operated for a total of 12 days, or 1460 PSA cycles, on the sour syngas. The guard beds accepted sour syngas for a total of roughly 625 hours. In addition to processing sour syngas, the PSA was operated for another 560 cycles on syngas that did not contain H2S (before breakthrough in the guard beds).

Five separate PSA operating points were characterized, two for syngas without H2S and three for sour syngas. In all cases, the PSA operated at a feed pressure of ~300 psig, then was depressurized and purged at about 5 psig. Performance results for one of the sour gas runs are listed below. The overall mass balance was within 1%, while component balances were within about 8%. The PSA rejected nearly all of the H2S (99.7%) and more than 95% of the CO2 in the feed gas. Product gas purity was maintained at 1.4 ppm H2S even though the feed level was around 250 ppm. The recovery of H2 to the product gas was 72%. Simulations are underway to compare the model predictions with these performance values.

Table 1. Summary of PSA Performance Data for PSA Operating Point #3.

MB3, In/Out		H2 recovery	72.1 %	feed	prod	dep/prg	
total	1.01	H2S rejection	99.7 %	H2	13.4	16.6	9.3
H2	0.99	CO2 rejection	95.4 %	N2	68.5	78.5	56.0
N2	1.00	1.4 ppm H2S in product		CO	2.2	2.9	1.5
CO	0.98			CO2	15.2	1.2	32.6
CO2	1.08			C1	0.72	0.85	0.51
C1	1.02			C2 ppm	38	9	86
C2	0.93			H2S ppm	256	1.5	610
H2S	1.02			COS ppm	<10	0	19

The PSA system appeared to yield the same performance when similar process setpoints were used at the beginning and end of the sour gas testing, suggesting that the adsorbent characteristics remained stable through that period.

After the syngas tests, another set of breakthrough runs were conducted, and the results showed a very modest 3% reduction in the CH₄ capacity and essentially no change in the H₂S capacity. These results are plotted in Figure 2 and support the observation of stable cyclic PSA performance.

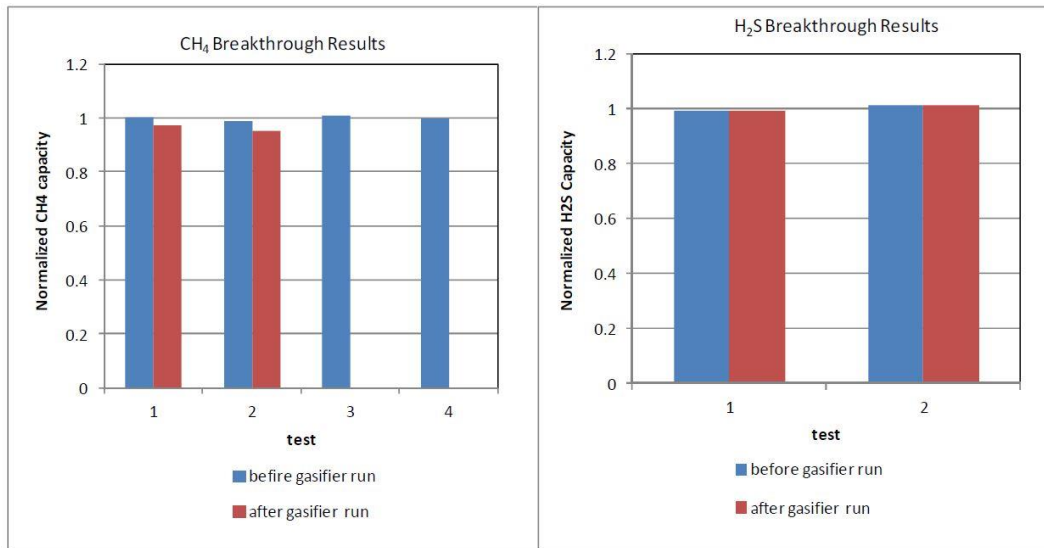


Figure 2. CH₄ and H₂S Breakthrough Capacities Obtained Before and After Gasifier Tests.