

Timothy C. Merkel (Primary Contact)
RTI
P.O. Box 12194
Research Triangle Park, NC 27709
merkel@rti.org
Tel (919) 485-2742
Fax (919) 541-8000

Brian S. Turk
RTI
P.O. Box 12194
Research Triangle Park, NC 27709
bst@rti.org
Tel (919) 541-8024
Fax (919) 541-8000

Raghubir P. Gupta
RTI
P.O. Box 12194
Research Triangle Park, NC 27709
gupta@rti.org
Tel (919) 541-8023
Fax (919) 541-8000

Daniel C. Cicero
U.S. Department of Energy
National Energy Technology Laboratory
P.O. Box 880
Morgantown, WV 26507
daniel.cicero@netl.doe.gov
Tel (304) 285-4826
Fax (304) 285-4403

Suresh C. Jain
U.S. Department of Energy
National Energy Technology Laboratory
P.O. Box 880
Morgantown, WV 26507
suresh.jain@netl.doe.gov
Tel (304) 285-5431
Fax (304) 285-4403

A Hybrid Gas Cleaning Process for Production of Ultraclean Syngas

Keywords: Desulfurization, Gasification, Sorbent, Polymer Membrane

Introduction

An important goal of the U.S. Department of Energy's (DOE's) VISION 21 Program Plan is to develop enabling technologies to convert fossil fuels into electricity and value-added chemicals. Current and growing reliance on imported oil and natural gas to meet the nation's electricity and transportation fuels need may endanger our economic future. DOE's VISION 21 Program Plan conceptualizes energy facilities that use advanced technologies to convert domestic solid carbonaceous fuels, primarily coal, into electricity and co-products (transportation fuels, chemicals, etc.) without impacting the environment. One of the enabling technologies specified in the VISION 21 Program Plan is "gas stream purification" for removing sulfur-, nitrogen-, chlorine-, and alkali-containing species to near-zero levels. During gasification of a carbonaceous feedstock, in an integrated gasification combined cycle (IGCC) system, fuel-bound contaminants naturally present in carbonaceous materials convert into gaseous impurities, such as H₂S, COS, NH₃, HCN, HCl, and alkali (sodium/potassium macromolecules). Depending on the temperature and pressure in various IGCC subsystems (syngas cooler, particulate control, and

gas and steam turbines, etc.), these gaseous species can pass directly through the particulate and sulfur control subsystems. For example, at temperatures above 1250°F, ceramic barrier filters will not capture alkali species. These alkali species are known precursors of corrosion-inducing condensates formed on gas turbine blades (Bachovchin 1986). Similarly, if reduced sulfur species (e.g., H₂S, COS) in syngas are not controlled, they can poison NH₃ decomposition catalysts downstream (Jothimurugesan and Gangwal 1998). Both sulfur and nitrogen species entering the gas turbine will be converted to SO_x and NO_x, which are known precursors of acid rain and whose emission into the atmosphere is regulated by federal, state, and local laws. Uncontrolled chlorine species might damage the sulfur control systems (by reacting with desulfurization materials) and can potentially induce corrosion of the turbine blades in an IGCC system.

In today's market-driven electric power production environment, the current high capital cost of IGCC systems (\$1,000 to \$1,200/kW) precludes their commercial deployment in the near future. The current low cost of natural gas in conjunction with the low capital cost of gas turbines (\$400 to \$600/kW) makes a natural gas combined cycle (GCC) system a more attractive option for power production than an IGCC system, or even a conventional coal-fired boiler. Furthermore, concerns over global climate change resulting from emissions of greenhouse gases (especially CO₂ from the use of solid carbonaceous fuels) have further decreased the merits of coal-fired systems. While IGCC systems are more efficient than coal combustion boilers, they generate significantly more CO₂ per kWh of electricity produced than a GCC system. Low interest in coal-based power production is leading to alternative applications of IGCC technology in fuel cell systems and the production of value-added chemicals.

Traditionally, natural gas (predominantly methane) has been used as a primary building block for producing H₂, methanol, Fischer-Tropsch liquids, and other value-added chemicals, and as the feed to fuel cells (molten carbonate, phosphoric acid, etc.). However, natural gas needs to be reformed into synthesis gas (containing CO and H₂) before it can be used for these applications. This is an energy intensive process. In an IGCC system, synthesis gas (or syngas) is the product of gasification of carbonaceous fuels, but this syngas needs deep cleaning to remove various contaminants before it can be used for H₂ and value-added chemicals production or in fuel cells. This paper reports on the status of technology development work to clean syngas to ultra-low contaminant levels.

Objective

The overall objective of this project is to develop technologies for cleaning/conditioning IGCC-generated syngas to meet contaminant tolerance limits for fuel cell and chemical production applications. The specific goals are to develop processes for (1) removal of reduced sulfur species to sub-ppm levels using a hybrid process consisting of a polymer membrane and a regenerable ZnO-coated monolith or a mixed metal oxide sorbent; (2) removal of hydrogen chloride vapors to sub-ppm levels using an inexpensive, high-surface-area material; and (3) removal of NH₃ with acidic adsorbents followed by conversion of this NH₃ into nitrogen and water.

Existing gasification technologies can effectively and efficiently convert a wide variety of

carbonaceous feedstocks (coal, petcoke, resids, biomass, etc.) into syngas, which predominantly contains carbon monoxide and hydrogen. Unfortunately, the impurities present in these carbonaceous feedstocks are converted to gaseous contaminants such as H_2S , COS , HCl , NH_3 , alkali macromolecules and heavy metal compounds (such as Hg) during the gasification process. Removal of these contaminants using conventional processes is thermally inefficient and capital intensive. This research and development effort is focused on investigation of modular processes for removal of sulfur, chlorine, nitrogen and mercury compounds from syngas at elevated temperature and pressures at significantly lower costs than conventional technologies.

Approach

Figure 1 shows a schematic of the overall process for removal of sulfur, chlorine, and nitrogen compounds from syngas. As illustrated, this approach consists of a number of different modular processes that can be integrated as needed to meet the different syngas conditioning requirements for fuel cell, chemical production, or power generation applications. It is envisioned that various individual modules can be used in a “mix and match” fashion depending on the type and level of contaminants and cleanup requirements.

In this process, raw syngas generated in a gasifier and cooled in a syngas cooler is fed to a fixed-bed reactor system for removing HCl and heavy metal vapors. HCl is removed from the syngas through reaction with an alkali carbonate supported on a relatively inexpensive, high-surface area support. Downstream of the HCl removal system, a hybrid system consisting of a polymer membrane module and a monolith (or a fixed-bed) desulfurizer removes the sulfur species from the syngas to sub-ppm levels. The last component of the syngas cleanup train is an NH_3 removal system based on selective adsorption of NH_3 on a highly acidic support material. A more detailed description of each of these processes is given in the following sections.

The target temperature for sulfur, HCl , and NH_3 removal processes is between 100 and 800°F, particularly in the 300 to 500°F range. This range is ideal for production of chemicals (such as methanol, Fischer-Tropsch products, and H_2) and also for phosphoric and solid oxide fuel cells. Furthermore, with a syngas cleanup temperature between 300 and 500°F, conventional filtration systems, such as bag filters and metallic barrier filters, can be used.

Project Description

Research Triangle Institute (RTI) is working with several industrial and academic partners to develop and commercialize the different technologies required for the various syngas conditioning steps. Each of these modular processes will now be discussed.

HCl Removal. RTI is collaborating with SRI International (SRI) to develop a relatively inexpensive alkali carbonate-based sorbent for the removal of HCl from raw syngas. Often, synthetic sorbents (chloride guards) are used in the chemical industry to reduce HCl vapor levels to extremely low levels. These sorbents are usually sodium compounds (typically sodium carbonate) impregnated on a high surface area support such as alumina ($\sim 200 \text{ m}^2/\text{g}$). The major drawback of these materials is that they are expensive (typically \$1 to \$2 per kg, resulting primarily from the high cost of the alumina support). This cost factor tends to preclude the use of commercial chloride guards in syngas applications.

As an alternative to the high cost of catalyst supports, several low cost and moderate surface area materials were considered as support media for the active ingredient, sodium carbonate. Such materials include (1) pyrolyzed rice hulls, (2) diatomaceous earth, and (3) sepiolite minerals. A bench-scale system is being used at SRI to determine the achievable residual HCl vapor level, the rate of chloride uptake as a function of time, and the maximum achievable chloride capacity of the sorbents.

Bulk Sulfur Removal. For the second stage of the syngas cleanup train, RTI is working with MEDAL (**ME**mbra**NE** **Du**Pont **Air** **Liquide**)—a joint venture between DuPont and Air Liquide (and a wholly owned subsidiary of Air Liquide) to develop and commercialize gas separation membrane technologies—and with North Carolina State University (NCSU) and University of Texas (UT) at Austin to develop polymer membrane technology for bulk removal of H₂S from syngas. These membranes are being specifically engineered to enhance the “solubility selectivity” of the membrane for removal of the acid gas components (H₂S, CO₂, NH₃, and H₂O) from syngas.

Commercial polymer membrane systems (e.g., air separation, H₂ recovery from NH₃ purge gas, and CO₂ removal from natural gas) are based on stiff chain rigid glassy materials, which exhibit high diffusivity selectivity. In these membranes, small penetrants permeate through the membrane faster than larger penetrants (Stern 1994; Freeman and Pinnau 1997). If this type of polymer were used for syngas conditioning, H₂ would easily pass through the membrane and collect in large concentrations on the low-pressure side of the membrane (permeate). However, recompression of this H₂-rich stream to feed pressure is economically prohibitive.

However, diffusivity selectivity is only one of the components affecting overall selectivity. The other component is *solubility selectivity*. The important factors affecting solubility selectivity are the relative condensability of the penetrants in the polymer matrix and the affinity of the penetrants for the polymer matrix. In solubility selective membranes, specific components from gas mixtures are separated based on their chemical properties and not their size, unlike in conventional diffusivity selective membranes such as cellulose acetate. If suitable polymeric membrane materials are developed to selectively permeate H₂S, CO₂, and other acid or polar gases (such as NH₃ and H₂O) from mixtures with light gases (such as H₂, CO, or N₂), this technology can become an attractive option for a host of applications requiring the removal of reduced sulfur species (such as H₂S, COS and CS₂) from syngas. Thus, the impurities in syngas could be removed and the desirable syngas components, namely H₂ and CO, could be maintained at high-pressure conditions as a non-permeate stream.

Sulfur Polishing. Removal of H₂S using a membrane is limited by the finite selectivity of the membrane for H₂S over H₂. Any additional sulfur removal from syngas required for fuel cell or chemical production applications will necessitate a sulfur polishing step. The current commercially available technologies used for polishing sulfur removal to sub-ppm levels are activated carbons, molecular sieve absorbents, disposable ZnO pellets, and newly available regenerable ZnO and zinc titanate pellets. However, because activated carbon and molecular sieve absorbents must be used at ambient temperature, applying them in the polishing sulfur removal process is problematic. Additional disadvantages include low activity, high cost, low sulfur capacity (typically <1 wt%), inability to remove low-boiling sulfur compounds such as COS, and

disposal of spent adsorbent. The economics associated with replacement and disposal of non-regenerable commercial ZnO absorbents prohibits the use of these absorbents for syngas applications. Although regenerable ZnO-based sorbents have low reactivity and limited capacity due to slow diffusion at temperatures below 500°F, recent advances make it possible to use these to lower the sulfur levels of syngas to sub-ppm levels (Turk and Gupta 2001). Alternatively, a monolith with a thin coating of high-surface-area zinc titanate (ZT) and/or ZnO materials could overcome the low reactivity, capacity limitations, and allow multiple regenerations. RTI is drawing upon its extensive expertise in desulfurization sorbents to exploring both of these routes as a means reduce to the residual sulfur concentration in the H₂-enriched stream leaving the membrane unit to sub-ppm levels.

Ammonia Removal. The final stage in the syngas cleanup is ammonia removal to < 10 ppmv. Although NH₃ is not a highly stable molecule thermodynamically ($G_f(298\text{ K}) = -3.9\text{ kcal/mol}$), the activation energy for dissociation is high (92 kcal/mol). Furthermore, the high concentration of H₂ in syngas, typical of that generated by slagging gasifiers, limits the level to which NH₃ can be reduced under equilibrium conditions by chemical decomposition (Gupta et al. 2000). According to extensive thermodynamic studies conducted by SRI, achieving a residual NH₃ level lower than 10 ppmv by catalytic decomposition will require operation at a temperature of 250°C (482°F) or below and conversion of significant amounts of H₂ to CH₄. Such low-temperature operation may not be feasible because of (1) the slow rate of reaction, and (2) potential condensation of steam.

An alternative removal process is to adsorb NH₃ on high-surface-area absorbents. In contrast to a catalytic decomposition process, the adsorption of NH₃ is facilitated at high pressure, but the quantity that can be adsorbed decreases at high temperatures. Molecular sieve sorbents have a high capacity for basic molecules such as NH₃. In these absorbents, the acid strength is often measured by its ability to adsorb a base, such as NH₃. The acidity of molecular sieves depends on various factors such as the composition, method of preparation, temperature of dehydration, and possible treatment with steam. RTI is working with SRI to optimize the performance of molecular sieve sorbents for NH₃ removal.

Results

HCl Removal. Moderate surface area pellets of diatomaceous earth and sepiolite powder were extruded in a bench-scale extruder with bentonite as a binder. The pellets were impregnated with a sodium carbonate solution and calcined at 450°C (842°F) in air. Pyrolyzed rice hulls were found to be too fragile, and severe gas channeling was observed, so this support material was not examined further.

The experimental sorbent granules were tested in the bench-scale reactor at about 350°C (662°F) and a space velocity of 2,000 h⁻¹ using a simulated gas containing 50 ppmv HCl vapor, 10% steam, 5% CO₂, and the balance N₂. Although this gas stream did not contain H₂ or CO, neither affects the uptake of HCl vapor by these sorbents. The observed results for sepiolite-based (S-01) and diatomaceous earth-based (D-01) sorbents are summarized in Table 1.

These results are encouraging in that they demonstrate that HCl vapor could be reduced to trace levels. The observed steady-state HCl levels are higher than equilibrium values, which could be

due to channeling of the gas through the bed. The sorbent utilization (the ratio of Na_2CO_3 converted to the initial amount of Na_2CO_3) might be improved by changing the impregnation and calcination procedures to provide an optimum pore size distribution. Although micropores contribute to the surface area, access to the interior of the micropores may limit the reactivity. Presence of both macropores and micropores are essential in optimizing the sorbent utilization. These changes could potentially increase the capacity of the sorbent for HCl uptake significantly.

Bulk Sulfur Removal. Initial membrane work was conducted at room temperature with a baseline material, polydimethylsiloxane (PDMS). PDMS is a highly permeable, rubbery polymer that is commercially used in membrane-based vapor separation applications. Its liquid-like polymer matrix has a poor ability to sieve molecules based on size, resulting in PDMS being more permeable to highly-soluble, condensable vapors than to small permanent gases. This suggests that PDMS will be more permeable to an acid gas like H_2S than to H_2 , a result that is desirable for our proposed syngas cleaning process.

Figure 2 presents the permeability coefficients of syngas components in PDMS at room temperature as a function of the gas critical temperature, T_c . In a solubility-selective polymer such as PDMS, there is often a strong correlation between the logarithm of gas permeability and T_c . Generally, as critical temperature increases, a penetrant becomes more soluble in the polymer and therefore more permeable, since permeability is equal to the product of solubility and diffusivity. The data in Figure 2 follow this trend, with the exception of hydrogen. This is often the case, as the extremely small molecular size of hydrogen results in a high diffusion coefficient and consequently a higher permeability coefficient than expected based on its T_c . Most importantly, the permeability coefficients of CO, H_2S , COS and SO_2 , for which almost no transport data exist, follow the general trendline through the other penetrants. This confirms that the permeation properties of these compounds are consistent with their molecular properties. Consequently, H_2S , COS, and SO_2 are more permeable than H_2 (and, in fact, considerably more permeable than CO_2) in PDMS and will preferentially permeate through the membrane. Additionally the high critical temperatures of H_2O and NH_3 indicate that these compounds will also be much more permeable than H_2 . Meanwhile, CO is less permeable than H_2 and will predominately be retained in the main syngas stream as is desired. Thus, the relative permeability of the main components of syngas in PDMS follow the trend: $\text{H}_2\text{O} \gg \text{SO}_2 > \text{COS} > \text{H}_2\text{S} > \text{NH}_3 > \text{CO}_2 \gg \text{CH}_4 \approx \text{H}_2 > \text{CO} > \text{N}_2$ (Merkel et al. 2001). These results demonstrate that a solubility-selective polymer can preferentially permeate H_2S (and other acid gases) over H_2 and CO, behavior which is critical for the membrane process to be economically viable. However, while PDMS is acid gas selective, its selectivities are not particularly high (e.g., $\text{H}_2\text{S}/\text{H}_2$ selectivity = 5.4, whereas a value of 40 is desirable). Consequently, a variety of novel polymeric materials have been examined.

Figure 3 summarizes the permeability-selectivity characteristics at room temperature of 17 polymer samples supplied by NCSU and MEDAL and tested at RTI. In this figure, membrane $\text{H}_2\text{S}/\text{H}_2$ selectivity is plotted as a function of film H_2S permeability. Ideally, it is desirable for a membrane to have high selectivity to maximize product purity and high permeability to minimize required membrane area. This difficult-to-attain, but advantageous combination of attributes corresponds to the upper-right-hand corner of Figure 3. The dashed line in this plot represents a permeability-selectivity “upper bound” which has been drawn to connect the

properties of PDMS (the highly permeable baseline polymer) and Pebax 4011 (a polymer with the highest acid gas selectivity previously reported in literature). As illustrated in Figure 3, several polymers tested at RTI (MEDAL 016, 018, and 023) exceed the upper bound line. This result represents significant progress in the development of acid gas selective membranes. As system temperature is increased, however, acid gas selectivities decrease systematically. For example, MEDAL 018 has a selectivity of 36 for $\text{H}_2\text{S}/\text{H}_2$ at ambient temperatures, but at 200°F the value is reduced to approximately 10. This behavior is typical for solubility-selective membranes where transport occurs by a solution-diffusion mechanism, and underscores the inherent difficulty in performing high temperature separations of this nature. In currently ongoing work, significant effort is directed towards improving the $\text{H}_2\text{S}/\text{H}_2$ selectivity at high temperatures by making chemical structure changes in the polymer materials. It also should be noted that all of the polymers described in Figure 3 exhibited excellent chemical and thermal stability, and that the MEDAL samples are suitable for production into hollow fiber modules of commercial size using the existing manufacturing technology at MEDAL.

Using a membrane simulator developed at NCSU (Coker et al. 1998), preliminary calculations were made to estimate the loss of H_2 and CO as a function of the extent of H_2S (or CO_2) removed from syngas. These simulations are based on the standard syngas composition, feed conditions, and the separation properties of MEDAL 018 at room temperature. Figure 4 presents the percent of inlet hydrogen that permeates the membrane as a function of the percent of inlet CO_2 that is removed in the permeate. Of course ideally, all of the CO_2 would be removed in the permeate without any H_2 loss through the membrane (corresponding to the bottom right corner of the plot). Since the membrane has a finite selectivity, there is a tradeoff, with the amount of hydrogen lost increasing as the amount of CO_2 removed increases. Figure 4 also presents operating envelope information regarding H_2S removal. This data is presented in the same manner as the CO_2 results with the addition of a second y-axis which describes the amount of H_2S remaining in the CO/H_2 enriched residue stream. As an example, if 80% of the inlet H_2S from syngas is removed, approximately 1500 ppm of H_2S in the H_2 -enriched syngas will be left, about 13% of the inlet H_2 will permeate the membrane, and 50% of CO_2 will be removed from syngas. Based on this membrane performance, 80 to 90% removal of H_2S from syngas is feasible without appreciable loss of H_2 and CO (Btu value). Additionally, this loss of H_2 and CO in the permeate stream is not really a loss in terms of overall thermal efficiency for an IGCC configuration since this stream can be used as a reductant for the Direct Sulfur Recovery Process (DSRP) and/or to heat the regeneration inlet gas for the monolith system. Various process design configurations, including use of a size-selective membrane to strip H_2 from the permeate stream of the solubility-selective membrane, are being considered to optimize heat integration.

Sulfur Polishing. For the polishing desulfurization, a number of ZnO -coated monolith materials were prepared and tested. The objective of this testing was to establish relationships between reactivity, surface area, and composition that will permit sulfur removal to sub-ppm levels at 150 to 260°C (300 to 500°F) and regeneration of the ZnO sorbents for multiple absorption/regeneration cycles. The first step towards developing a ZnO -coated monolith for this type of polishing desulfurization application began with screening combinations of different washcoat materials, ZnO loadings, and preparation conditions to enhance sulfur removal reactivity and capacity for cordierite monolith. Extensive thermogravimetric (TGA) testing of various formulations was conducted to identify superior materials for bench-scale testing. Several

superior formulations were subsequently tested to evaluate sulfidation reactivity as a function of temperature. Results of this TGA screening testing are reported elsewhere (Gupta et al. 2000).

The optimum formulations identified during the TGA screening tests were used to prepare 2-in diameter monolith samples for testing in RTI's HTHP bench-scale reactor system. Testing of these monolith samples began with a multicycle test at 1000°F, 280 psig, and a space velocity of 2,000 h⁻¹ (at STP). Over the first four cycles, the feed H₂S concentration was varied between 2,500 and 10,000 ppmv during sulfidation. The effluent sulfur concentrations and percent sulfur removal in Table 2 show that the monolith required several cycles for the desulfurization activity to fully develop and stabilize. This increase in desulfurization activity over the initial cycles or activation was previously observed during the TGA screening tests and is frequently required with regenerable sorbents.

In the next sequence of testing, the monolith temperature during sulfidation was reduced by roughly 100°F during each subsequent cycle. The other operating conditions were identical to those used in the previous 4-cycle test. The sulfur loading and average prebreakthrough effluent sulfur concentrations are shown as a function of sulfidation temperature in Table 3. Decreasing sulfidation temperatures were observed to have little or no effect on the effluent sulfur concentration down to temperatures as low as 200°F. However, the potential sulfur loading of the monolith was observed to decrease from roughly 12 wt% above 700°F to about 2 wt% below 400°F.

In the next sequence of testing, the objective was to explore the potential effluent concentration limits for the ZnO-coated monoliths. The breakthrough profiles for four sulfidations in this testing series are shown in Figure 5. Based on these data, effluent sulfur concentrations of < 0.5 ppmv (500 ppbv) can readily be achieved. The ability to achieve this level of desulfurization was dramatically influenced by regeneration conditions and performance. Additional testing is currently being conducted to improve the desulfurization performance to consistently achieve effluent sulfur concentrations <100 ppbv, by optimizing sorbent composition and regeneration conditions.

Although monoliths are one potential candidate for regenerable polishing desulfurization materials, fixed-bed regenerable sorbent materials could also be used. Advances in the formulation and preparation of these materials have increased desulfurization activity at lower temperatures and the ability to reduce effluent sulfur concentrations to sub-ppmv levels. The results from a multicycle test with the RVS-1 sorbent are shown in Figure 6. This RVS-1 sorbent was developed by the researchers at DOE/NETL and has been extensively evaluated for a number of syngas desulfurization cases (Turk and Gupta 2001). The operating conditions of testing this sorbent in this particular case were 450 psig, a target sorbent bed temperature of 520°F and a space velocity of 2,000 h⁻¹. After sorbent activation in the first cycle and the decomposition of trace amounts of sulfate formed during regeneration, RVS-1 could readily reduce effluent sulfur concentrations to below 1 ppmv even at steam concentration >60 vol% and a temperature of about 500°F.

In summary, both monoliths and fixed-bed sorbents have demonstrated the ability (1) to reduce effluent sulfur concentrations to <1 ppmv, (2) to maintain desulfurization performance after

regeneration for multiple cycles, and (3) to operate at lower sulfidation temperatures, potentially as low as 200°F. Research continues to increase desulfurization activity and capacity at lower temperatures and reduce the effluent sulfur concentrations for both the monoliths and fixed-bed sorbents. Regeneration conditions and activity are also being studied to minimize side reactions, particularly sulfate formation, to optimize regeneration.

Ammonia Removal. In this task, a temperature-programmed reactor was used to determine the adsorption and desorption behavior of NH_3 on selected sorbents. NH_3 was adsorbed at 225°C (437°F) by using pulses of a gas stream containing 5,000 ppmv NH_3 . The adsorption capacity was calculated from the differences in the feed and exit gas NH_3 concentrations. Subsequently, the catalyst containing adsorbed NH_3 was heated to desorb the NH_3 .

Three molecular sieves were selected for experimental determination of NH_3 adsorption and desorption studies. They are H-mordenite (LZ M-8), Y-type zeolite (LZY-62), and rare-earth exchanged Y zeolite (SK-500). The LZY-62 catalyst was treated with NH_4Cl to exchange the sodium present in the catalyst with H^+ ions. It was washed until no chloride was detected in the washwater. The catalyst was dried and calcined at 400°C (752°F) to remove any adsorbed NH_3 .

A temperature-programmed desorption reactor was used to determine the performance of catalysts for NH_3 adsorption and desorption under atmospheric pressure conditions. A small amount of catalyst was placed inside the reactor and was heated in N_2 to a temperature of 225°C (437°F). After temperature stabilization, pulses of 5,000 ppmv NH_3 in N_2 were introduced and the residual NH_3 levels were recorded. The capacity of the catalyst for NH_3 adsorption was calculated from the differences in the feed and residual levels. When the residual levels of NH_3 reached a value close to the feed gas value, the catalyst was heated at about 10°C/min to 500°C (932°F) while monitoring the desorbed NH_3 levels. Table 4 summarizes these results.

As seen in Table 4, the NH_3 adsorption capacities of these catalysts at 225°C (437°F) are somewhat lower than reported in the literature for H-mordenite catalyst (0.75×10^{-3} mol/g). The differences might be a result of using different vendors or pretreatment procedures. The ZSM-5 type molecular sieves were procured from Zeolyst International. These materials have very high acidity ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 50$ to 280) and high surface areas (400 to 425 m^2/g). They were heated to 400°C (752°F) to desorb moisture and subsequently exposed to pulses of 5,000 ppmv NH_3 at 225°C (437°F). The adsorption capacity of ZSM-type zeolites was similar to that of H-mordenite ($\sim 0.4 \times 10^{-3}$ mol/g), and the desorption temperature was about 350°C (662°F).

Application

The modular gas cleaning technology described in this paper, when fully developed, is expected to reduce the cost of gas cleaning significantly, thus, reducing the overall capital and operating costs of future IGCC systems. Preliminary estimates from a technical and economic evaluation done by Nexant, Inc., indicated that the capital cost of a hybrid desulfurization system is about 50% lower than the compared amine system, based on the Rectisol process.

Future Activities

RTI and its partners have made significant progress in advancing the syngas cleanup technology through laboratory and bench-scale development of various underlying processes. Economics

assessment of this technology indicates significant potential of further cost reduction in various areas, which are currently being addressed in Phase II research.

In bulk desulfurization, work will continue on screening the polymer samples being developed at MEDAL and UT, with particular emphasis on improving polymer selectivity for acid gases over H_2 and to improve its retention at elevated temperatures. MEDAL will prepare bench-scale membrane modules (about 1 ft² area) out of their most promising polymer materials. These modules will undergo extensive bench-scale testing at RTI to determine the intrinsic separation properties and their comparison with permeation properties of the films tested so far. Plans are also being made to produce a 150 ft² membrane module to test it with a real syngas in 2004.

On the polishing desulfurization, R&D work will continue to further lower the sulfur concentration in the syngas by optimizing the regeneration conditions and sorbent compositions. Both monolithic materials as well as fixed-bed pellets will be investigated for this application.

For the HCl removal system, a two-stage process may be more prudent than a single stage. Most of the HCl removal (down to about 1 ppmv) is done in the first stage using the previously developed nahcolite-based sorbents, which possess high chloride capture capacity. In the second stage, the chloride level is reduced to < 10 ppbv using the supported sorbents. This type of integrated system will be developed and tested in Phase II of this project.

For NH_3 removal system, a high-pressure fluidized-bed reactor system is being set up for cyclic adsorption and desorption studies. This reactor system will be used to screen various adsorbent compositions under simulated syngas conditions.

Pilot-scale testing of some or most of the process modules is also planned in 2004 with a slipstream of real syngas. Results of this pilot-scale testing will provide a realistic cost estimate for a commercial system based on this technology.

Acknowledgements

The work reported in this paper was performed with the sponsorship of the United States Department of Energy's National Energy Technology Laboratory (DOE/NETL) under contract No. DE-AC26-99FT-40675. HCl and NH_3 removal work reported in this paper was performed under the guidance of Dr. Gopala Krishnan of SRI International. Dr. Greg Fleming directed the polymer sample selection and preparation work at MEDAL, while Professor Benny D. Freeman was the principal investigator for the work performed at NCSU and UT. Prototech company custom prepared the ZnO coated monolith modules.

References

- Bachovchin, D. M. (1986). A Study of High Temperature Removal of Alkali in a Pressurized Gasification System, Westinghouse Research and Development Center.
- Coker, D. T., B. D. Freeman, et al. (1998). "Modeling Multicomponent Gas Separation Using Hollow Fiber Membrane Contactors." American Institute for Chemical Engineers Journal **44**(6): 1289-1302.

- Freeman, B. D. and I. Pinnau (1997). "Separation of Gases using Solubility-Selective Polymers." Trends in Polymer Science **5**(5): 167-173.
- Gupta, R. P., B. S. Turk, et al. (2000). Gaseous Contaminant Control for IGCC Applications. 17th Annual Pittsburgh Coal Conference, Pittsburgh, PA.
- Jothimurugesan, K. and S. K. Gangwal (1998). "Regeneration of Zinc Titanate H₂S Sorbents." Industrial & Engineering Chemistry Research **37**(5): 1929-1933.
- Merkel, T. C., B. S. Turk, et al. (2001). "Mixed Gas Permeation of Syngas Components in Poly(dimethylsiloxane) and Poly(1-trimethylsilyl-1-propyne) at Elevated Temperatures." Journal of Membrane Science **191**: 85-94.
- Stern, S. A. (1994). "Polymers for Gas Separations: The Next Decade." Journal of Membrane Science **94**: 1-65.
- Turk, B. S. and R. P. Gupta (2001). Development and Experimental Results on RVS-1 Desulfurization Sorbent. RTP, NC, Research Triangle Institute.

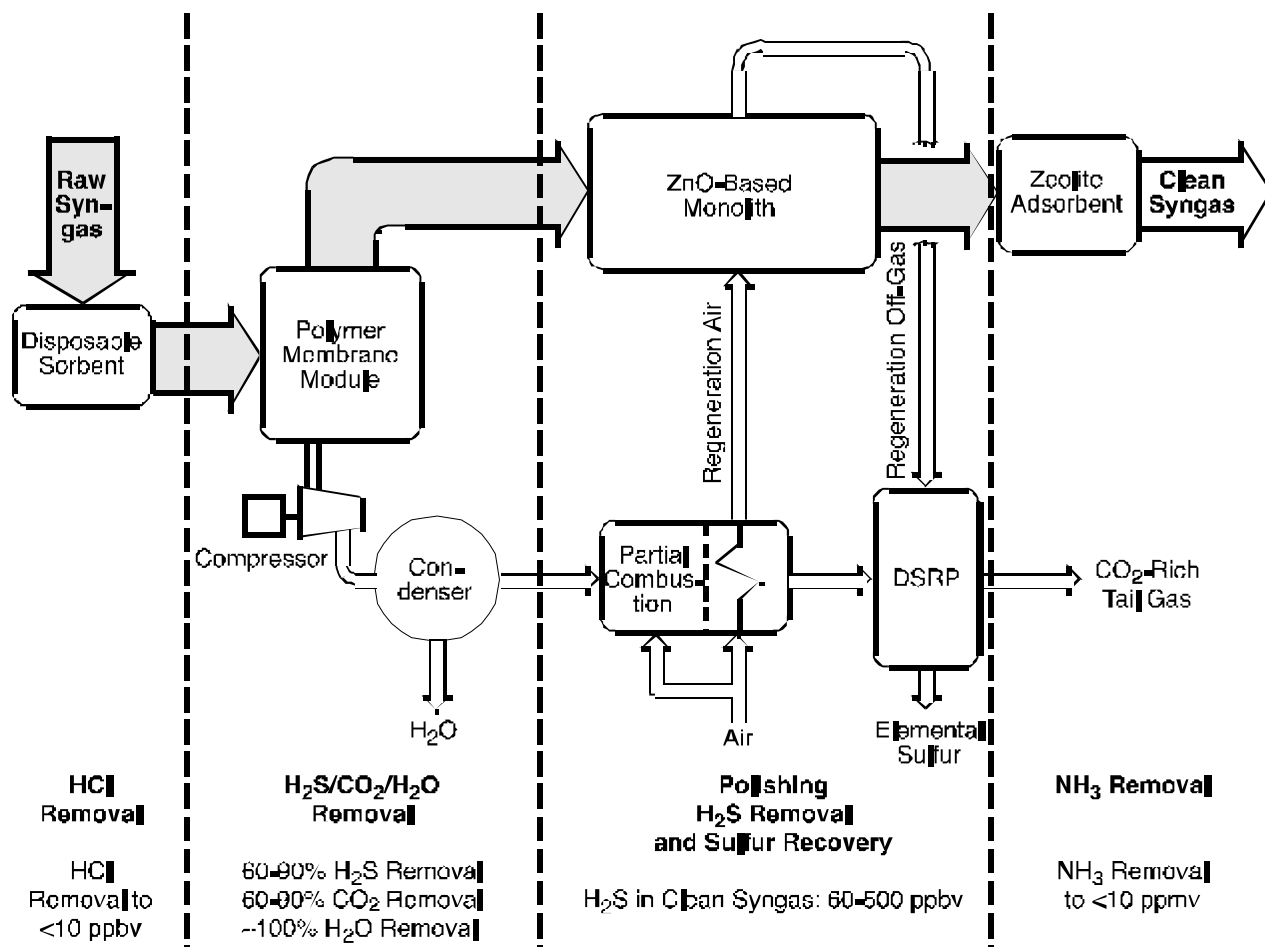


Figure 1: Schematic of overall process for IGCC contaminant control.

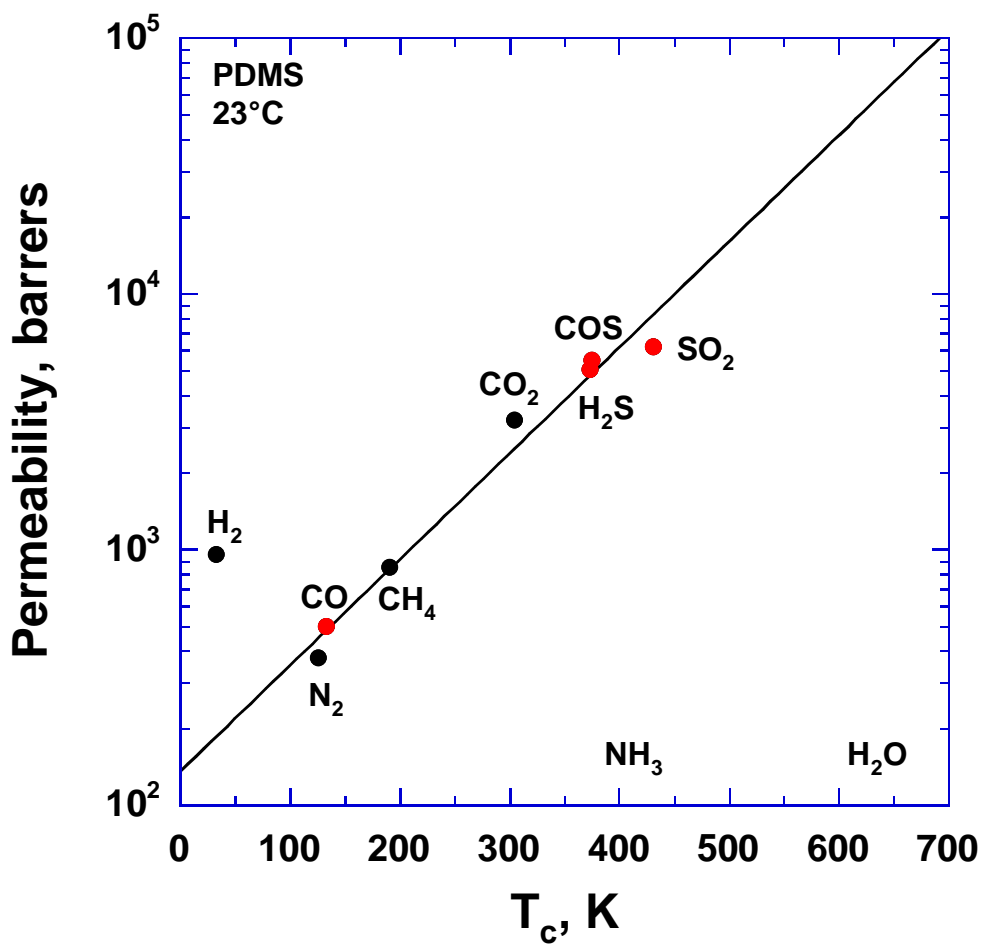


Figure 2: Syngas permeability in PDMS as a function of gas critical temperature.

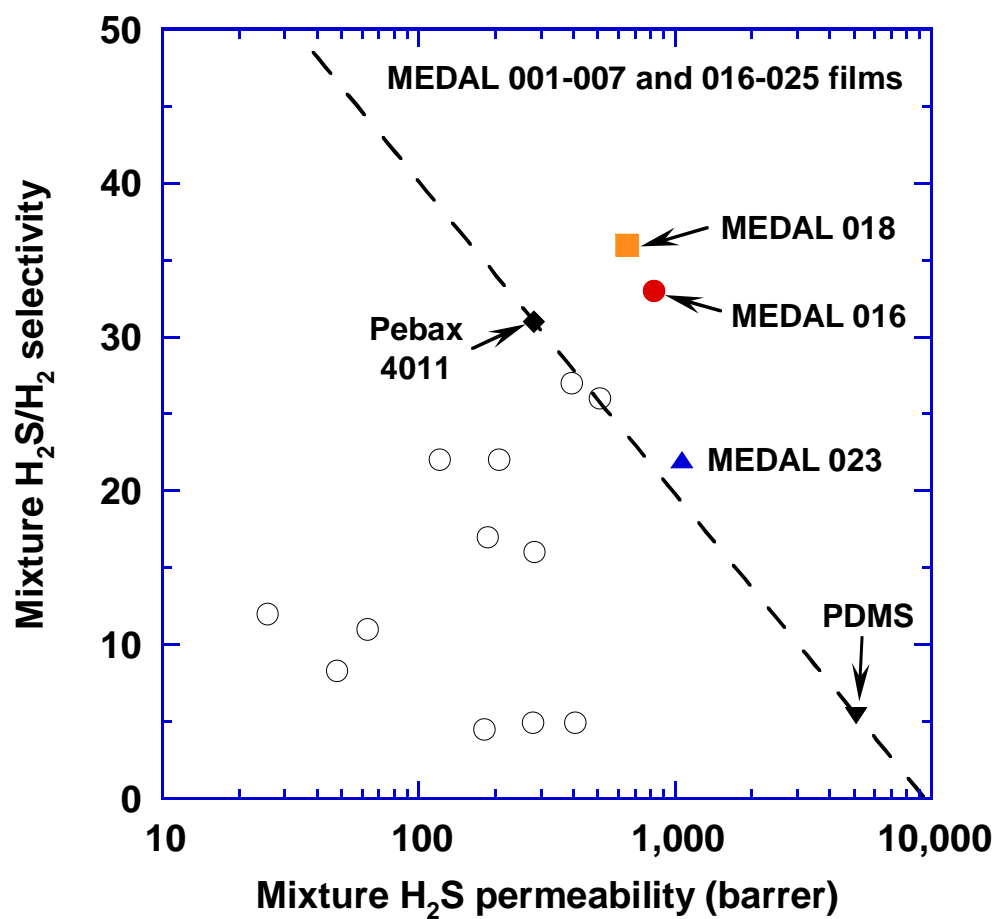


Figure 3: Mixed gas H_2S/H_2 selectivity as a function of H_2S permeability.

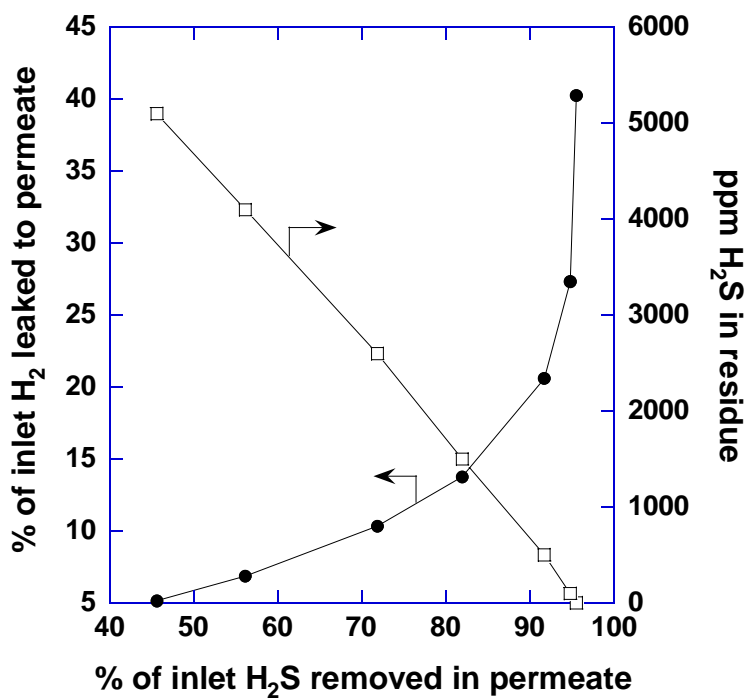
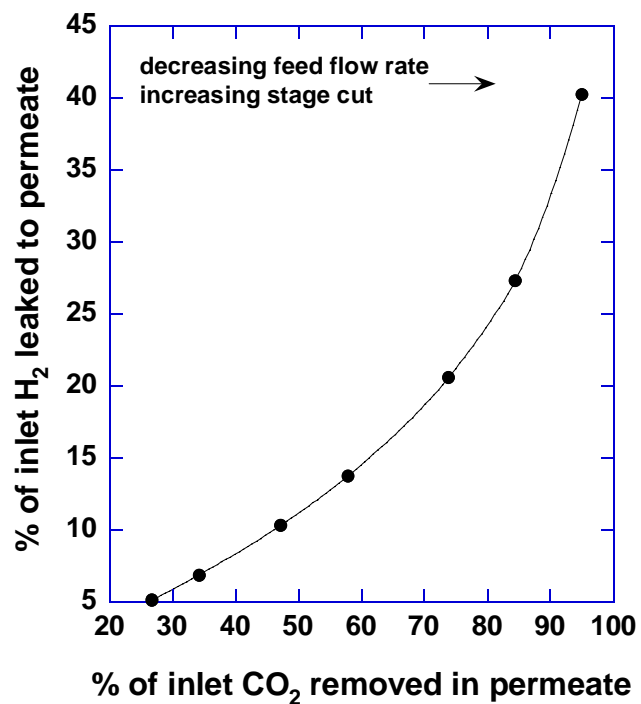


Figure 4: H₂ in permeate stream as a function of CO₂ and H₂S removal.

Table 1. Results of HCl Vapor Removal Experiments		
Property	S-01	D-01
Surface area (m ² /g)	98.3	10.8
Wt% Na ₂ CO ₃	5.1	1.08
Steady-state HCl level	35	80
Time for 0.1-ppm breakthrough (h)	40	10
Percent sorbent utilization	18.8	13.0

Table 2. Changes in Desulfurization Performance during Monolith Activation		
Feed H₂S (ppmv)	Effluent Concentration (Prebreakthrough, ppmv)	Sulfur removal (%)
10,000	39.7	99.60
5,000	9.7	99.81
2,500	1.0	99.96
5,000	1.5	99.97

Table 3. Effects of Desulfurization Temperature on Effluent Sulfur Concentrations and Sulfur Loading		
Sulfidation Temperature (F)	Effluent Concentration (Prebreakthrough, ppmv)	Sulfur Loading (wt%)
970	1.50	14.12
870	4.00	14.77
770	6.90	14.09
670	4.70	12.31
570	3.80	10.78
480	3.00	4.80
380	1.80	2.50
300	3.30	2.10
200	0.30	2.80

Table 4. Properties of Molecular Sieves for NH₃ Adsorption			
Property	LZM-8	LZY-62	SK 500
Surface area (m ² /g)	450	650	520
SiO ₂ /Al ₂ O ₃ (mol)	17.1	2.4	4.9
NH ₃ adsorption at 225°C (437°F) (mol/g)	0.4 x 10 ⁻³	0.35 x 10 ⁻³	0.25 x 10 ⁻³
Peak desorption temperature (°C)	395	Broad	Broad