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Conf-920951--53

DOE/MC/26372-93/C0103

Development of Hollow-Fiber Catalytic-Membrane Reactors for High-Temperature Gas Cleanup

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DOE/MC/26372--93/C0103

DE93 004086

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Contract Number:
DE-AC21-89MC26372

Conference Title:
Twelfth Annual Gasification and Gas Stream Cleanup
Contractors Review Meeting

Conference Location:
Morgantown, West Virginia

Conference Dates:
September 15-17, 1992

Conference Sponsor:
U.S. Department of Energy, Morgantown Energy Technology Center

DISCLAIMER

Development of Hollow-Fiber Catalytic-Membrane Reactors for High-Temperature Gas Cleanup

CONTRACT INFORMATION

Contract Number	DE-AC21-89MC26372
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METC Project Manager	V. K. Venkataraman
Period of Performance	March 21, 1991 to July 31, 1992

Schedule and Milestones

FY91-92 Program Schedule

	A M J J A S O N D J F M A M J J A S
Catalyst Deposition on Membrane	----------
Catalyst Activity Investigation	----------
Gas Permeation and Reaction Studies	----------
Membrane Quartz Reactor Construction	----------
Alumina Membrane Reactor Installation	----------

OBJECTIVES

The goal of the project is to develop catalytic membrane reactors for IGCC gas cleanup at high temperatures and pressures. The objectives of this research and development effort are: (i) characterization of raw fibers and investigation of their permeability and thermal behavior, (ii) introduction of catalytic compounds on the hollow fiber and their characterization, and (iii) evaluation of catalytic membrane reactors for their performance in facilitating the decomposition of hydrogen sulfide in pure component and gas mixture systems.

BACKGROUND INFORMATION

The use of a catalytic-membrane reactor for high-temperature gas cleanup is attractive due to its advantage of integrating reaction and separation within membrane reactors. Application of catalytic membrane reactors for the removal of H_2S from IGCC gas mixture will improve the performance of advanced power systems. Utilizing the zinc ferrite and calcium-based sorbents in the gas cleanup process has benefited the removal of H_2S. Other techniques that directly remove H_2S by catalytic decomposition, recovering H_2 and sulfur, provided added economic advantage.

H_2S decomposition catalyzed by transition metal sulfides, such as MoS_2 and V_2S_3, has been reported [1,2]. However, the decomposition of H_2S with formation of H_2 and sulfur is thermodynamically unfavorable at low temperatures. One approach to increase the conversion is the removal of H_2 or sulfur from reaction products. The degree of H_2S conversion can be improved by using inorganic membranes to separate H_2 from the gaseous mixture. A two-fold increase in H_2S conversion above the equilibrium level was reported in porous glass membranes [3] and in an alumina membrane [4].

Hollow fiber glass membranes have advantages over typical ceramic membranes. The fine porous, silica-rich fibers provide a large surface area to volume ratio in module design and good selectivity for gas separations. Ideal separation factors calculated by using the ratio of pure gas permeabilities much higher than for conventional inorganic membranes were reported [5]. Our prior work, during earlier stages of the project, showed that a measured separation factor for CO_2 to N_2 was 20 in a gas mixture at ambient temperature [6]. The development of catalytically active hollow fiber membranes has potential for increasing the conversion in H_2S decomposition which is otherwise limited by its thermodynamic equilibrium.

PROJECT DESCRIPTION

The project consists of the following main activities:

(1) Design of catalytic hollow fiber membrane reactors. Single and multiple hollow-fiber membranes were studied in reactor/permeation cells made from stainless steel or quartz tubes. Modification of the hollow fiber membrane with catalysts was performed by aqueous impregnation, vapor deposition, and utilization of packed-bed reactors.

(2) Investigation of gas separations and catalytic reactions in membrane reactors. Permeation of pure gases and gas mixtures was studied as a function of temperature. Pure component catalytic studies on the decomposition of H_2S was typically studied using 10% H_2S diluted in He. The H_2S and H_2 concentrations were measured in both the tube and shell sides of the membrane reactor to determine the degree of chemical equilibrium shift.

(3) Process development of the cleanup system using a simulated gas stream with a composition similar to that from an IGCC system. Catalytic studies using the IGCC gas composition will be performed according to the procedure used in the H_2S experiments. The conditions for optimum conversion in a gas mixture will be investigated.

RESULTS

Permeation Cell and Catalytic Reactor

The reactor/permeation cells were constructed from stainless steel or quartz tubes and consisted of single or multiple hollow fibers with a shell-and-tube arrangement. Stainless steel (s.s) tubes with 1.59×10^{-3} m OD have been used for permeability studies at temperatures below 400°C. Quartz (q) tubes with 3×10^{-3} m OD and 1×10^{-3} m ID were used especially for the catalytic studies at elevated temperatures. Chromatography fittings (Chromlok™, SGE) and graphite ferrules were used for metal to quartz connections. Epoxy resin was used for sealing fibers to metal/quartz tubes. The hollow fiber membrane (with ID 20μm, OD 31μm) used in the project was supplied by PPG Industries, Inc. The pore surface areas were in the range of 3×10^5 to 4×10^5 m^2/kg, and pore volumes were in the range of 8×10^{-5} to 1.5×10^{-4} m^3/kg.

Experimental Apparatus

A schematic diagram of the experimental setup, shown in Figure 1, presents different feeding and sampling systems for the permeation and catalytic studies. Feed and purge gases were alternatively flowed through the tube or shell side of the reactor. The valves at the outlet and inlet of the reactor allowed desired samples of feed, permeate, or lumen to be delivered to the GC.

Gas flows were controlled by electronic mass flow meters. An Omega readout/controller was used to regulate the temperature in the range of 30 - 1000°C. The system pressure was maintained by a metering valve at the reactor outlet. In H_2S decomposition studies, a sulfur scrubber was used to remove sulfur at the reactor outlet.

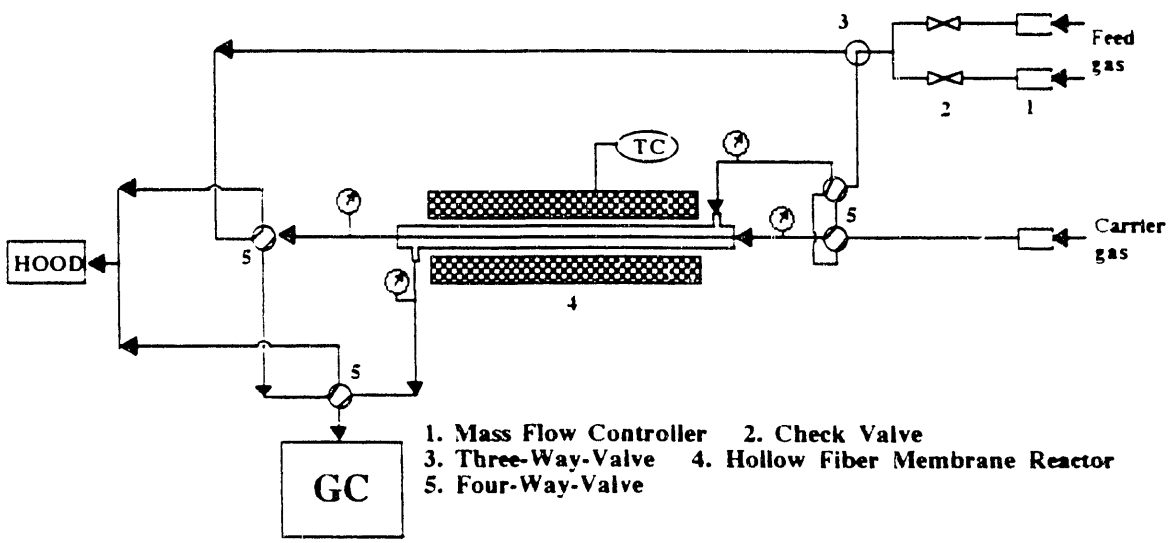

Figure 1. Schematics of the Experimental Setup

Preparation of Catalytic Hollow Fiber Membranes

Preparation of the catalytic hollow fiber membranes was first performed in a single fiber membrane (s.s) reactor. Molybdenum compounds were initially deposited on the inside surface of the hollow fiber via aqueous impregnation or vapor deposition methods. The deposited membrane was calcined in air or N_2 from ambient temperature to 300°C and then treated with a flowing stream of 1% H_2S in H_2 at 350°C.

Solutions of ammonium molybdate (0.1 - 0.0001 M) were used as precursors in aqueous impregnation. Vapor deposition was carried out by purging sublimed molybdenum hexa-carbonyl through the lumen of the fiber in a N_2 flow. A decrease in N_2 permeability was observed during and after the catalyst deposition. The SEM results showed that the reduction in permeability during the process was mainly due to the accumulation of Mo components at the fiber entrance. However, all the preparations, resulted in failures of the fibers during the subsequent calcination or sulfidation treatments, due primarily to a reduction in strength of the fiber by deposited catalyst.

Alternatively, a packed-bed reactor configuration was employed by packing catalysts in the shell side of the reactor. The catalysts used in this study were as follows. MoS_2 (Johnson Matthey, metal basis) and Pt/Al_2O_3 (Aldrich, 5 wt%) were used as received. $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (Mallinckrodt) was pretreated by calcination and sulfidation; $Mo/Co/P/Al_2O_3$ (Cyanamid) was sulfided prior to the H_2S decomposition study.

Permeation of Gases

Permeability data for N_2, Ar, CO_2, and C_2H_4 in the membranes have been previously reported [6]. Continuing studies focused on the permeation of H_2 and H_2S.

Permeability studies of H_2S and H_2 mixture were carried out in multiple fiber (q) reactors. The feed gas was introduced from the shell side of the reactor and permeate gas exited from the tube side without using any carrier gas. The shell side pressure was maintained in a range of 50-53 psig, while, the pressure at the outlet of the tube side of the reactor was near the ambient pressure. Figures 2 and 3 show flow rates and separation

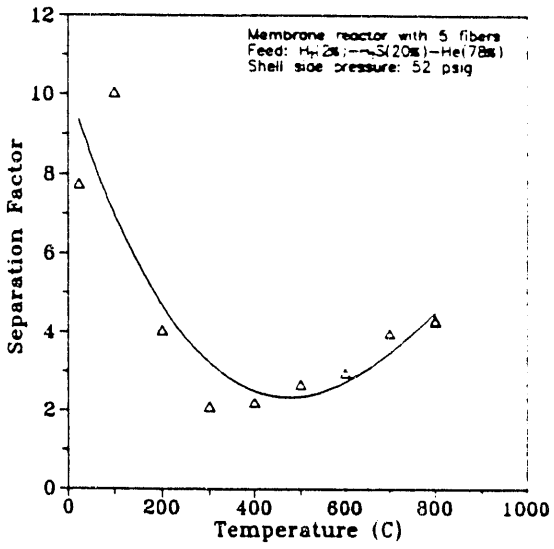

Figure 2. Variation of H_2/H_2S Mixture Separation Factor with Temperature for 20% H_2S.

factors as a function of the temperature for a gas mixture consisting of 20 mol% H_2S, 2 mol% H_2, and 78 mol% He. Net permeate flow rate and separation factor increased as the temperature increased. Initially, however, further increases (> 100 °C) in temperature resulted in a reduction of permeation rate and separation factor. Similar results were also observed in a mixture containing 1 mol% H_2S and 35 mol% H_2 in He (see Figure 4). These results indicate that the net permeate flow rate could be reduced at elevated temperatures.

The observed effect of decreasing the transmembrane flow with temperature can be

explained based on the model of compressible flow in the hollow fiber lumen. As the temperature increases, gas viscosity increases, causing greater friction losses for gas flow inside the fiber. A mathematical model describing the process of mass transport in hollow fiber membranes at elevated temperatures has been developed in the Center for Inorganic Membrane Studies, WPI and will be applied to depict the system under study in our forthcoming reports.

H_2S Decomposition

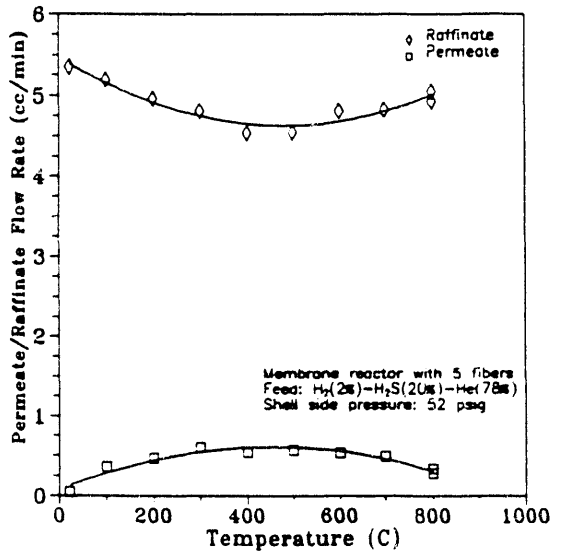

Figure 3. Permeate and Raffinate Flow rates versus Temperature.

The theoretical H_2S equilibrium conversions, calculated at different temperatures, pressures, and concentrations are shown in Figure 5. Less than 10% conversion of pure H_2S is expected at 800°C. Dilution of H_2S stream increases the conversion.

A higher conversion may be obtained by the removal of products selectively from the reaction zone [3,4]. In the present study, multiple hollow fiber membrane reactors were developed to facilitate H_2 removal in H_2S decomposition. A feed containing 10.5 mol% H_2S diluted in He was used. Catalysts were packed in the shell side of the reactors where the feed stream was introduced. The exit of the permeate flow near the entrance of the shell side was sealed. Permeate gases exited from the other side without using any carrier gas.

Several H_2S decomposition studies were carried out in membrane reactors constructed from stainless steel tubes. Ammonium molybdate and $Mo/Co/Pt/Al_2O_3$ catalysts were used. The initial studies in stainless steel reactors resulted in a nearly quantitative removal of H_2S at 800°C. Subsequent studies in stainless steel reactors containing no catalyst resulted in high H_2S disappearance at 800°C. This study showed that stainless steel itself became quite active at even higher temperatures; thus, this phase of the study turned to examining the reaction in quartz reactors. A comparison of H_2S thermal decomposition carried out in stainless steel and quartz reactors is shown in Table 1.

Table 1. Conversion of H_2S (mol.%) in Stainless Steel and Quartz Reactors without Catalyst

T °C	Stainless Steel	Quarz	Equilibr. Conversion (calc.)
500	6.35	<0.01	1.15
700	21.47	0.45	7.45
900	63.01	3.6	23.45

Investigations of H_2S decomposition in quartz reactors packed with MoS_2 and Pt/Al_2O_3 catalysts have been carried out. Figure 6 shows the activity of these catalysts as a function of pressure and residence time at 800°C. MoS_2 exhibited

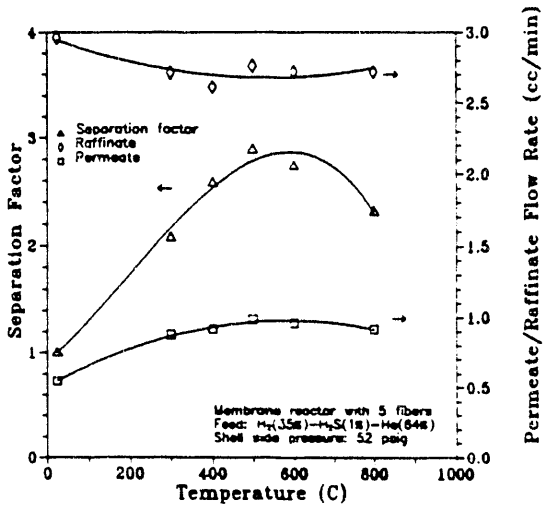

Figure 4. Variation of H_2/H_2S Mixture Separation with Temperature for 1% H_2S.

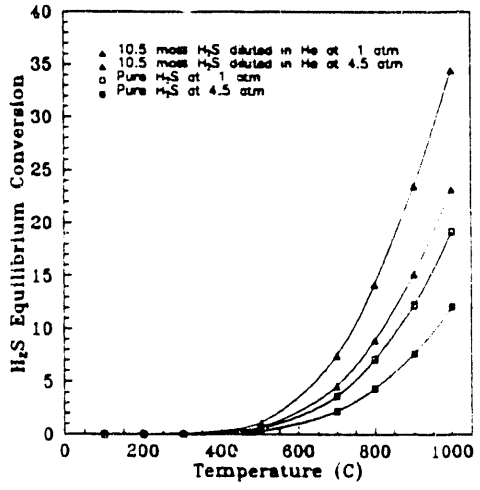

Figure 5. Theoretical values of H_2S equilibrium conversion.

fairly good activity and resulted in essentially equilibrium conversions. The activity of MoS_2 is higher than Pt/Al_2O_3. The H_2S conversion over $Pt/Al2O_3$ was dependent on the residence time.

The H_2S decomposition in multiple fiber quartz reactors was investigated. It was found that the Epoxy was not stable at elevated reaction temperatures. A rapid decrease in the permeate flow or a termination of the tube side flow occurred when the temperature rose above 700°C. This resulted from either a failure of the Epoxy seal or the blockage of the fiber by solid sulfur. The use of cooling air at the exit of the reactor to prevent the failure of the Epoxy, might have resulted in the formation of solid sulfur leading to blockage of the lumen of the fiber. Improvement

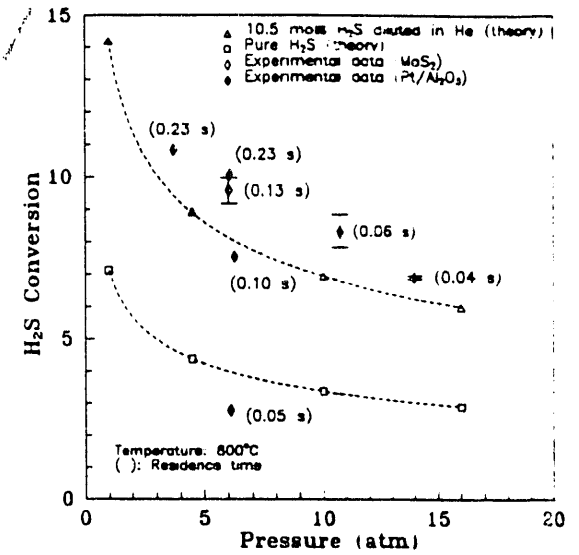

Figure 6. Catalytic Activity in H_2S Decomposition.

of high temperature seals in progress.

FUTURE WORK

In the coming year, the following activities have been planned:

- Further improvement of the high temperature seals for the quartz reactor.

- Completion of the permeation studies at high temperatures for simulated gas with gas composition similar to that from an IGCC system.

- Evaluation of other commercial catalysts in

the 700-900°C temperature range to determine the maintenance of their catalytic activities.

- Application of active catalysts in a hollow fiber packed-bed reactor.

- Study of the degree of equilibrium shift for H_2S decomposition in the membrane reactor.

- Examination of the optimum conditions for H_2S conversion in an IGCC gas mixture.

- Theoretical modeling, economic analysis and scale up.

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