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DEVELOPMENT OF HOLLOW FIBER CATALYTIC MEMBRANE REACTORS FOR HIGH TEMPERATURE GAS CLEANUP

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9b.5 Development of Hollow Fiber Catalytic Membrane Reactors for High Temperature Gas Cleanup

CONTRACT INFORMATION

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Period of Performance	4/93- 3/94

FY94 Program Schedule

OBJECTIVES

The *objective* of this project was to develop economically and technically viable catalytic membrane reactors for high temperature, high pressure gaseous contaminant control in IGCC systems. These catalytic membrane reactors were used to decompose H_2S and separate the reaction products. The reactors were designed to operate in the hostile process environment of the IGCC systems, and at temperatures ranging from 500 to 1000 °C.

BACKGROUND INFORMATION

The technology employed in the Integrated Gasification Combined Cycle (IGCC) permits burning coals with a wide range of sulfur concentrations. Emissions from the process should be reduced by an order of magnitude below stringent federal air quality regulations for coal-fired plants. The maximum thermal efficiency of this type of process can be achieved by removing sulfur and particulates from the high temperature gas (e.g., 800 °C to 900 °C). High temperature sulfur removal can be accomplished with sorbents or by using membrane reactors. Catalytically active membrane reactors offer an inherent ability to combine reaction, product concentration and separation in a single unit operation. The conversion of H_2S is limited by the thermodynamic equilibrium of the reaction but can, in principle, be improved by the removal of products (e.g., H_2) during reaction. Here, selective removal of hydrogen could be provided by the membrane during reaction so that the reaction is continuously driven toward the product side. As the membrane is more permeable to H_2, the reaction can be almost shifted to complete conversion.

PROJECT DESCRIPTION

The membrane reactor is an integrated process which includes membrane and reactor processes in a single unit operation. Therefore, to ensure a proper design of the membrane reactor several components of the process should be analyzed including:

- membrane gas permselectivity and thermal stability;
- hydrodynamics of gas flow at elevated temperatures;
- thermodynamics of H_2S decomposition;
- reaction rates of homogeneous and heterogeneous reactions of H_2S decomposition;
- membrane reactor design;
- H_2S decomposition in the membrane reactor at different operational parameters.

Based on experimental information on the H_2S conversion in the membrane reactor, a mathematical model was developed providing an adequate (within 5%) description of the process. The model provided information on the best operation parameters of the membrane reactor process.

RESULTS

Severe conditions encountered in the IGCC process (e.g., 900 °C, H_2S, CO_2 and H_2O) make it impossible to use polymeric membranes in the process. Therefore, inorganic membranes were used in the design of the membrane reactor - molecular-sieve glass membrane and Vycor glass porous membrane.

Membrane permselectivity

The molecular-sieve glass membrane acquired from PPG Industries Inc. was found far superior to polymeric counterparts in terms of the selectivity, permeability and thermal stability. Temperature dependencies of gas permeability in the molecular-sieve membrane is presented in Figure 1. Separation of gases in the microporous membrane occurs according to configurational diffusion mechanism developed in [1-4]. Even though the selectivity coefficients of the molecular-sieve glass membrane are very attractive for separation of H_2 at room temperature ($\alpha[H_2/H_2S] \approx 200$) the selectivity decreases with the temperature and at 800 °C is approximately 10. This selectivity is approximately two times higher than the selectivity coefficient for Knudsen diffusion mechanism. In addition, the porous structure of the membrane collapses at temperatures higher than 300 °C and gas permeability irreversibly decreases (Figure 2).

On the other hand, the permeability of the Vycor glass membrane remains unchanged up to a temperature of 850 °C. The selectivity factor in the Vycor glass membrane is independent of the temperature and is equal to $\alpha[H_2/H_2S]=4.1$. Even though the selectivity coefficient is lower than for the microporous glass membrane, the Vycor glass membrane was used for the design of the high temperature membrane reactor because of its thermal stability.

Experimental installation

A schematic diagram of the experimental installation used in this study is presented in Figure 3. Quartz tubes with OD/ID=16/13 mm were used as the reactor shells. One end of the membrane was fixed to the quartz tube with epoxy resin Duralco 4525 (Cotronics) stable up to a temperature of 250 °C. The other end of the membrane was sealed with the same epoxy. The feed gas mixture was supplied on the shell side of the membrane reactor. The furnace was 15 cm long. The porous glass membrane and the quartz tube were 30 cm long. The length of the permeable part of the membrane in the membrane reactor was equal to 22 cm. The temperature in the furnace was controlled by a thermocontroller. The gas composition on the shell and the tube sides of the membrane reactor was analyzed with a Hewlett Packard HP5890 GC. The pressure in the sampling loop was controlled with a specially designed vacuum gas sampling system to provide reliability and accuracy in a wide range of gas concentrations. The reactor ends were cooled by air flow to prevent overheating and decomposition of the epoxy resin. Flow rates on the feed and shell sides were measured with a bubble flowmeter. The pressure on the shell side of the membrane reactor was kept at either 2.36 atm or 7.8 atm while the pressure on the permeate side of the membrane was kept atmospheric. Before the experimental runs the system was kept at 800 °C in a feed gas flow for 24 hours.

Hydrogen concentration

The stage cut for the membrane reactor is similar to the stage cut for the conventional membrane reactor and is defined as the ratio of the permeate flow to the sum of the permeate and reject flows according to

$$\mathit{Stage\ Cut} = \frac{\mathit{Permeate}}{\mathit{Permeate} + \mathit{Reject}}$$

During the membrane reactor operation hydrogen produced during the reaction of H_2S decomposition was selectively removed through the Vycor glass membrane and concentrated on the permeate side (Figure 4). When the stage cut increased the concentration of H_2 on both the permeate and reaction sides decreased. At the stage cut equal to one the concentration of H_2 on the permeate side is equal to the equilibrium concentration of H_2 for the reaction of H_2S decomposition at 1 atm. Similarly, at stage cut equal to 0 the concentration of H_2 on the reaction side is equal to the equilibrium concentration of H_2 for the H_2S decomposition reaction at 7.8 atm. Similar dependencies of the H_2 on the stage cut were observed when 100%, 1%, and 500 ppm H_2S gas mixtures were used as a feed.

H_2S conversion

From the definition of the stage cut it follows that at the stage cut equal to 0 the effect of H_2 removal from the reaction gas mixture is negligible and cannot affect the total conversion in the membrane reactor. As the stage cut increased the effect of H_2 removal increased as well. At the stage cut equal to one, the total conversion in the membrane reactor is equal to the total conversion on the low pressure or permeate side of the membrane reactor (Figure 5).

Noteworthy, that even though the stripping of H_2 from the reaction side occurred in the membrane reactor the total conversion did not increase compared to the equilibrium conversion in the packed bed reactor. Therefore, the membrane with the Knudsen selectivity of gas separation appears to be not suitable for enhancement of the conversion in the membrane reactor.

Mathematical model

A mathematical model was developed to simulate the performance of the membrane reactor. Comparisons between theoretical predictions and experimental data are shown in Figure 4. A good agreement between the experimental data and simulations was also observed for feed mixtures with a different content of H_2S.

The developed model was used to predict the optimum conditions at which the conversion of H_2S can be conducted to the highest degree of the conversion. When the membrane with selectivity coefficients higher than those of the Knudsen selectivity is used in the membrane reactor the conversion may be considerably higher than the conversion in the conventional packed bed reactor (Figure 6). The best results were obtained when the selectivity coefficients are equal to 500-1000 with respect to H_2 separation. Such high selectivity coefficients are difficult to get at temperatures equal to 800 °C even in the molecular-sieve membranes.

Additionally the effect of downstream pressure on the total conversion in the membrane reactor was analyzed. It was demonstrated that only when the absolute pressure on the permeate side is lowered down to 0.01 atm the high conversions (up to 90%) of H_2S can be achieved.

FUTURE WORK

A comprehensive analysis of the membrane reactor demonstrated that under certain conditions the membrane reactor may provide high conversions at low stage cuts. These conditions include high membrane selectivity (100 times the Knudsen selectivity) and low pressure on the permeate side (0.01 atm). it is not recommended to use sweep gas in any part of the membrane reactor because hydrogen in the permeate will be diluted and can not be utilized. The conversion in the membrane reactor can increase only if highly selective membrane is used such as Pd or Pt and low pressures on the permeate side are kept. The conversion can be further increased if simultaneously a higher pressure on the reaction side is applied to lower a pressure ratio (pressure ratio = downstream pressure/upstream pressure) and to improve the membrane separation performance.

The membrane reactor processes appears to be more appropriate for processes with high contents of the reactant material. It can be used in gas phase reactions whose components are difficult to separate. The membrane reactor unit operation in this case provides simultaneous reaction and separation in a single technological unit.

CONCLUSIONS

* Feasibility of the membrane reactor process for decomposition of hydrogen sulfide was demonstrated.

* Permeability and selectivity of molecular-sieve and Vycor glass membranes were studied at temperatures up to 1000 °C.

* Experimental study of hydrogen sulfide in the membrane reactor was completed.

* A generalized mathematical model was developed for the simulation of the high temperature membrane reactor.

* The efficiency of the membrane reactor process is probably lo for the high temperature clean-up of H_2S from the IGCC gas mixture.

* Knudsen selectivity is insufficient to yield an increase of the H_2S conversion in membrane reactor.

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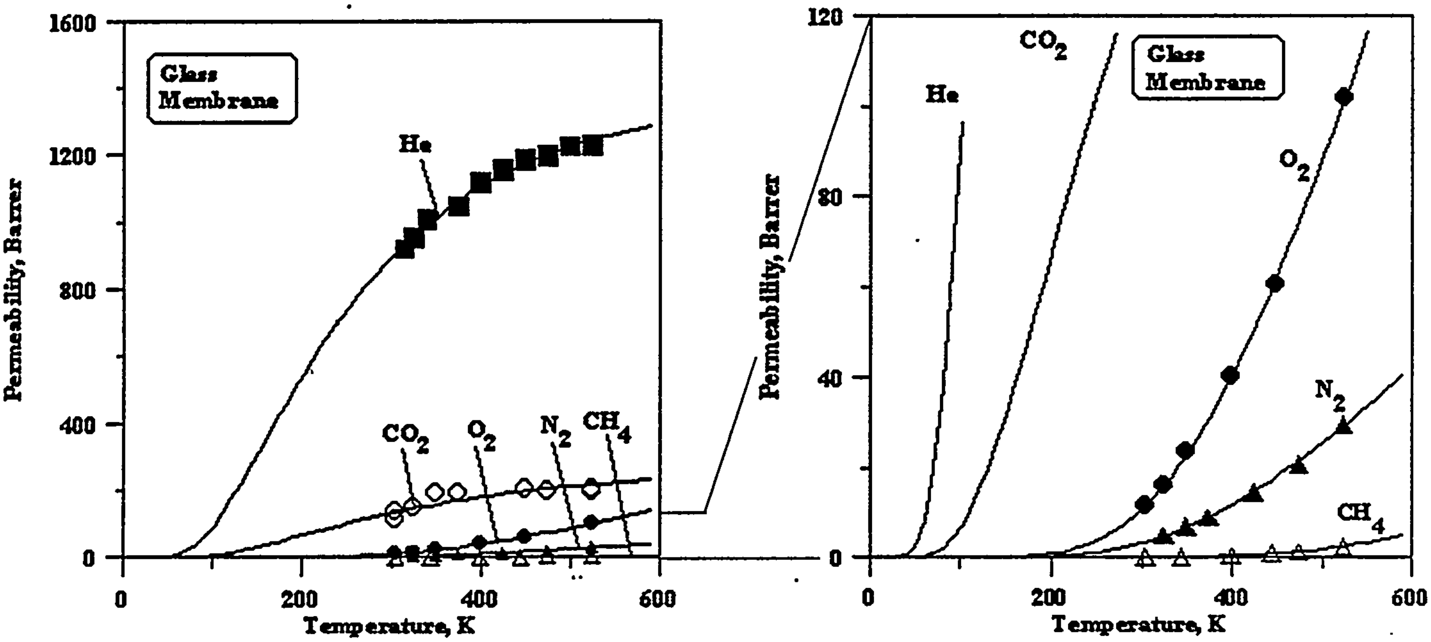


Figure 1 Permeability of molecular-sieve glass membrane.

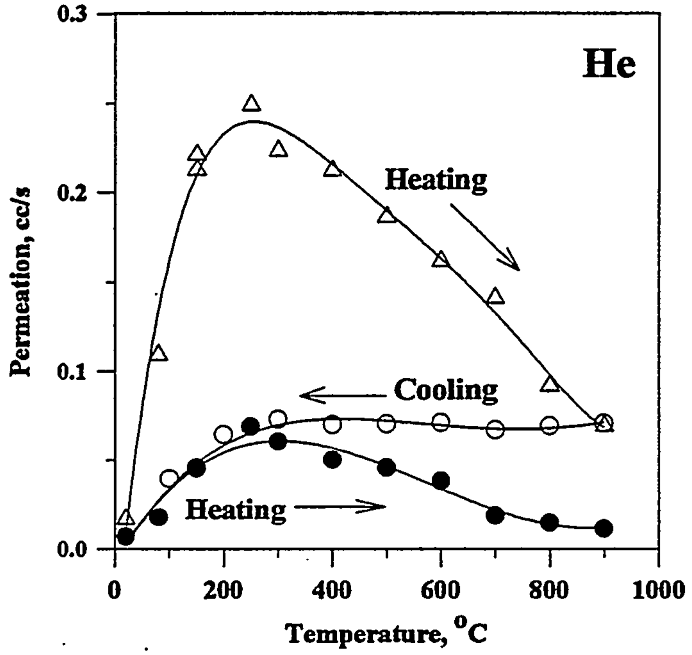
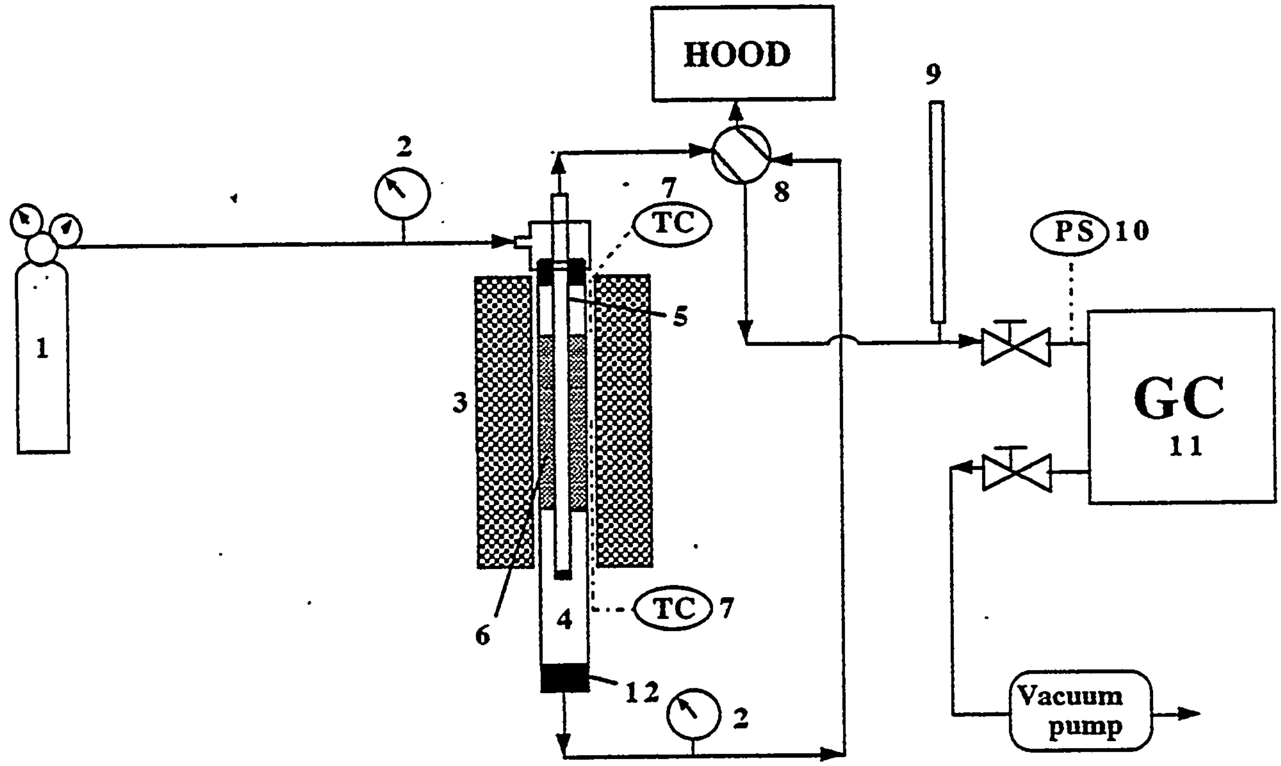


Figure 2 Temperature stability of molecular-sieve glass membrane.



1- Feed, 2- Pressure gage, 3- Furnace, 4- Membrane/packed-bed reactor, 5- Porous Vycor glass membrane, 6- Catalyst (MoS_2), 7- Thermocouple, 8- 4-way-valve, 9- Bubble flow meter, 10- Pressure sensor, 11- Gas chromatograph, 12- Epoxy resin.

Figure 3. The schematic diagram of the experimental installation.

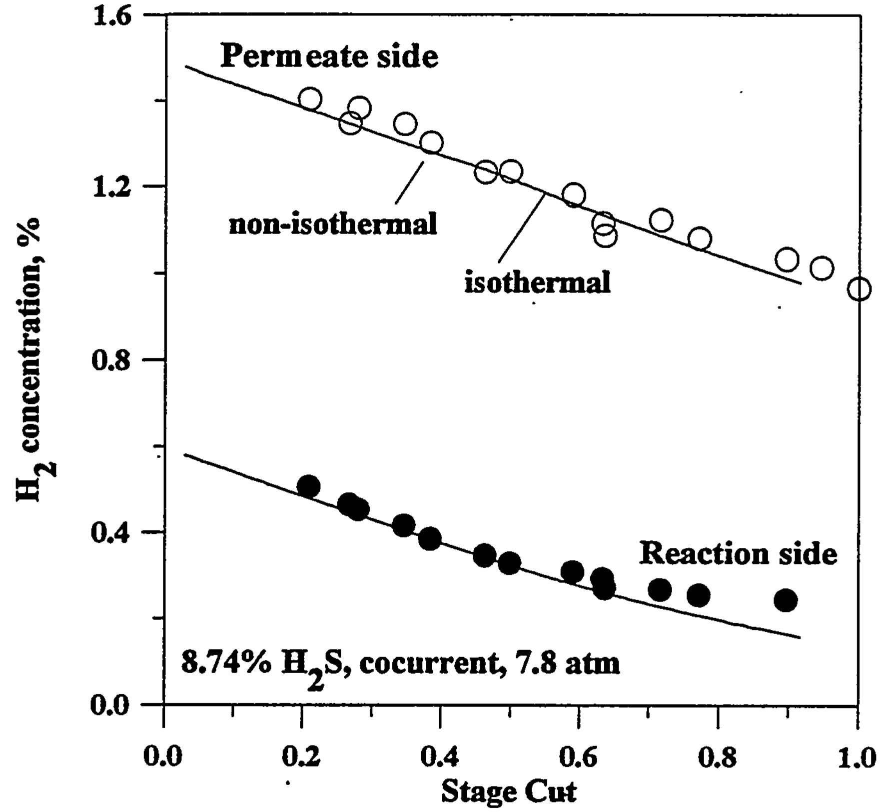


Figure 4 Concentration of hydrogen at the permeate and rejection side outlets in the membrane reactor.

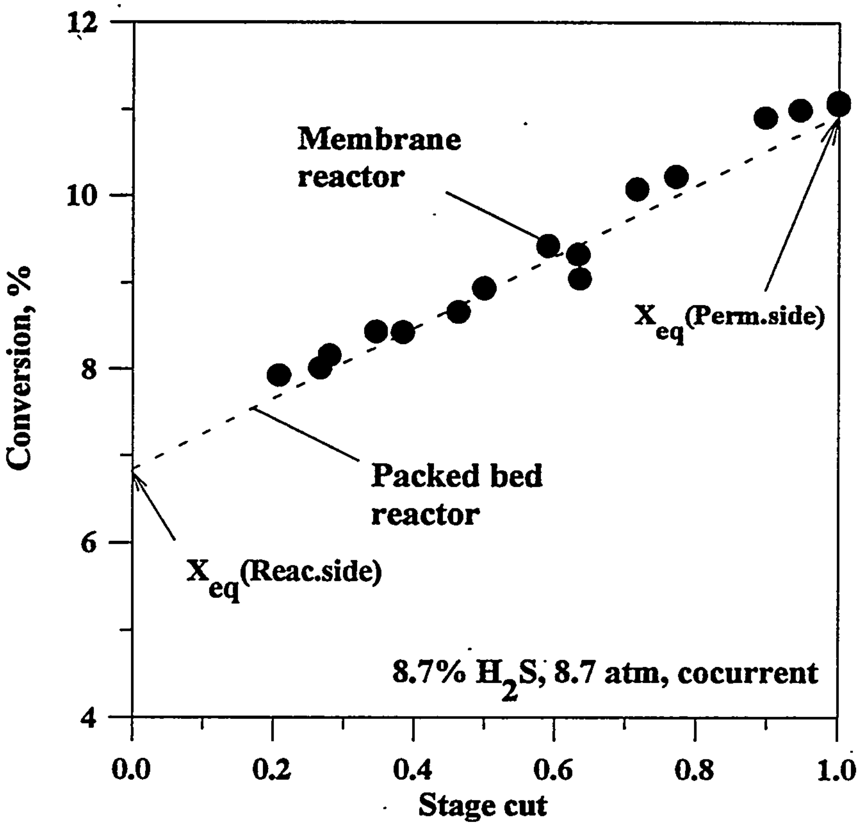


Figure 5 Total conversion of H_2S in the membrane reactor.

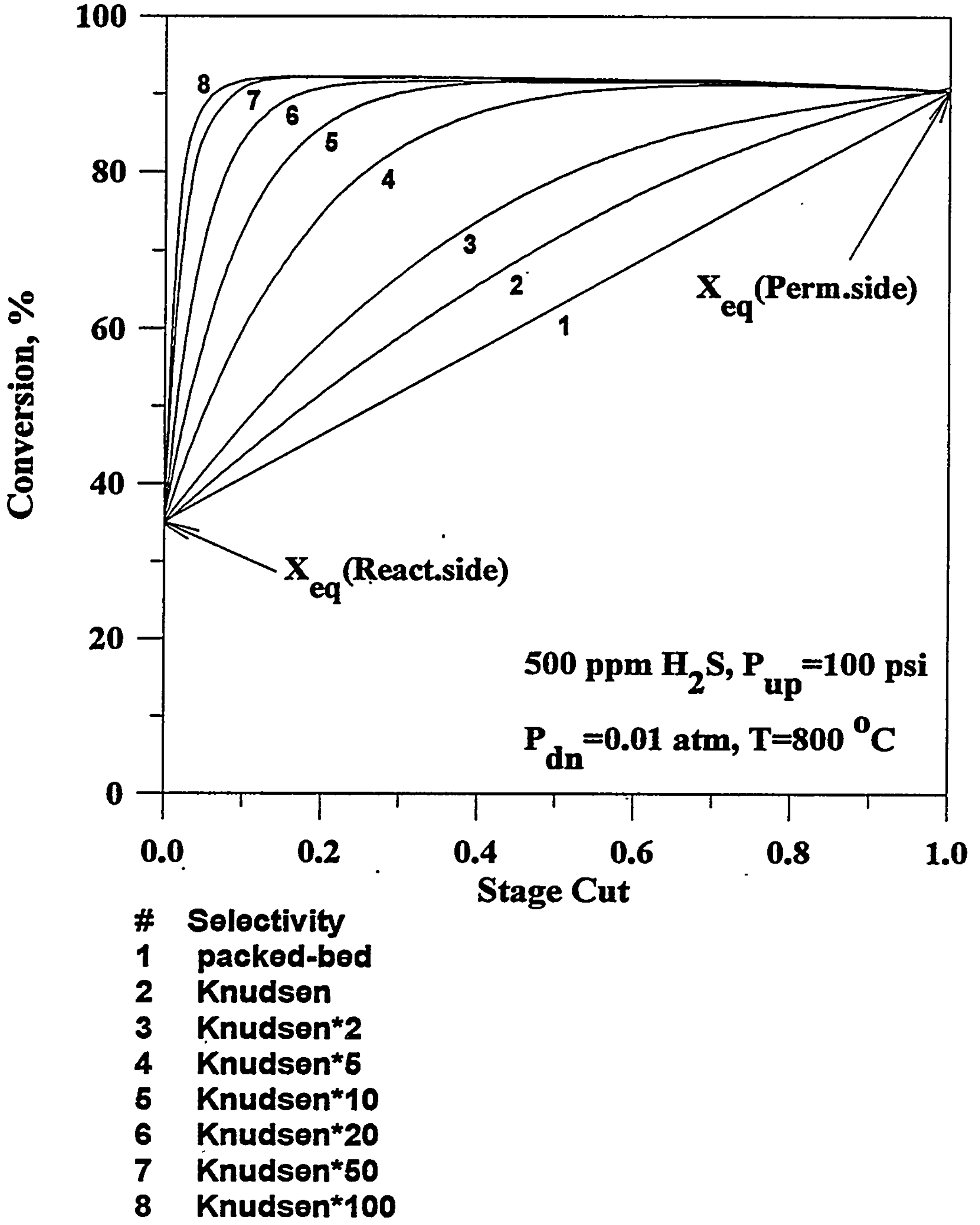


Figure 6. Effect of the membrane selectivity on the total conversion of H_2S in the membrane reactor.