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EXPERIMENTAL EVALUATION OF DEHYDROGENATIONS USING CATALYTIC MEMBRANE PROCESSES

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ABSTRACT

Many industrially important dehydrogenation reactions are operated under conditions where the equilibrium conversion is limited by the production of hydrogen. Ceramic membrane reactors offer the potential for increased conversion at existing operating temperatures or reduced operating temperature for the same conversion level by removal of product hydrogen.

This paper reports the results of recent efforts to develop catalytic membrane reactors for the dehydrogenation of ethylbenzene to styrene. The focus of this study was to compare the performance of a hybrid reactor, consisting of a packed bed followed by a membrane reactor, with that of a traditional two-stage packed-bed reactor under industrially relevant conditions. The hybrid configuration mimics the simplest implementation of a ceramic membrane reactor, simulating the use of the membrane reactor as an add on stage to the existing reactor train.

A benchscale system has been developed that is capable of experimentally simulating the industrial operation. Features of this system include syringe pumps from which an ethylbenzene liquid hourly space velocity of 0.4 hr^{-1} is attainable with a water:ethylbenzene molar ratio of 9, a 7-zone furnace in which isothermal catalyst bed temperature profiles within ± 1°C are achieved, and two dual FID/TCD on-line gas chromatographs for simultaneous analysis of the entire spectrum of compounds in the permeate and reject effluents from the reactor with 30 minute analysis turnaround time. The membrane module incorporates a four-point thermocouple in the catalyst bed to insure isothermal operation and three single-point thermocouples on the permeate side for monitoring purposes.

Results obtained with this system showed a 4% yield enhancement to styrene in the hybrid reactor compared to the traditional two-stage packed bed. This enhancement was achieved with no loss in styrene selectivity. Carbon deposition on the membrane was observed during reaction which rapidly reduced the permeability from 70 $m^3/m^2/hr/atm$ for the fresh membrane to a value of 2 $m^3/m^2/hr/atm$ under reaction conditions. This 2 $m^3/m^2/hr/atm$ permeability was a steady state value representing a dynamic equilibrium between coke formation from organic compounds and coke removal due to the presence of steam in the reaction mixture and was constant for run times in excess of 100 hours.

INTRODUCTION

Microporous ceramic membranes have been the subject of growing interest for a variety of separations. Details of their synthesis, characterization and application have recently been summarized (1). One area of particular interest has been the application of these materials for high temperature gas separations. This is due to their excellent stability under severe thermal and chemical environments compared to their organic polymer counterparts. One application of significant potential is the use of ceramic membranes as chemical reactors where controlling the concentration of one or more reactants or products is important.

Catalytic dehydrogenations are an important class of reactions where product yields are thermodynamically limited by the formation of H_2 in the catalyst bed. The dehydrogenation of ethylbenzene to produce styrene is a major commercial process where this is the case. Ceramic membrane reactors have been the focus of several studies to effect the in situ removal of this H_2 in order to enhance styrene yields (2-4).

This paper reports the results of recent efforts to develop a membrane reactor for the dehydrogenation of ethylbenzene to styrene using a commercially available ceramic membrane. The focus of these efforts is to assess the impact of the membrane under realistic industrial conditions. Towards that end, a system was designed that closely duplicates the industrial process. Initial experimental results obtained from that system indicate that styrene yields can be enhanced with no loss in styrene selectivity using the commercial ceramic membrane under industrially relevant conditions. Future work will focus on optimizing the performance of the membrane reactor.

EXPERIMENTAL

The reaction system used in this study is shown schematically in Fig. 1. Water and ethylbenzene liquids are fed to vaporizers via variable flow Harvard Apparatus syringe pumps. These pumps can deliver the liquid feed rates of approximately 20 μL/minute necessary to achieve LHSVs of 0.4 hr^{-1}. The vaporizers are of thermosyphon design. In the lower section, large volumes of vapor are generated. Much of this flow condenses in a cold arm on the side. A large circulating flow of vapor is thus set up. A small portion of this recirculation is drawn through a needle valve on the top of the vaporizer and fed to the system. Ethylbenzene and water vapor are carried to the reactor by flowing N_2.

The membrane reactor is housed in a seven-zone furnace. Three zones heat the preheater section and four zones are localized around the membrane module. The four zones around the module can be independently adjusted to yield an isothermal temperature profile along the membrane reactor. Temperature profiles within ±1°C are routinely achieved. A N_2 purge is provided on the permeate side of

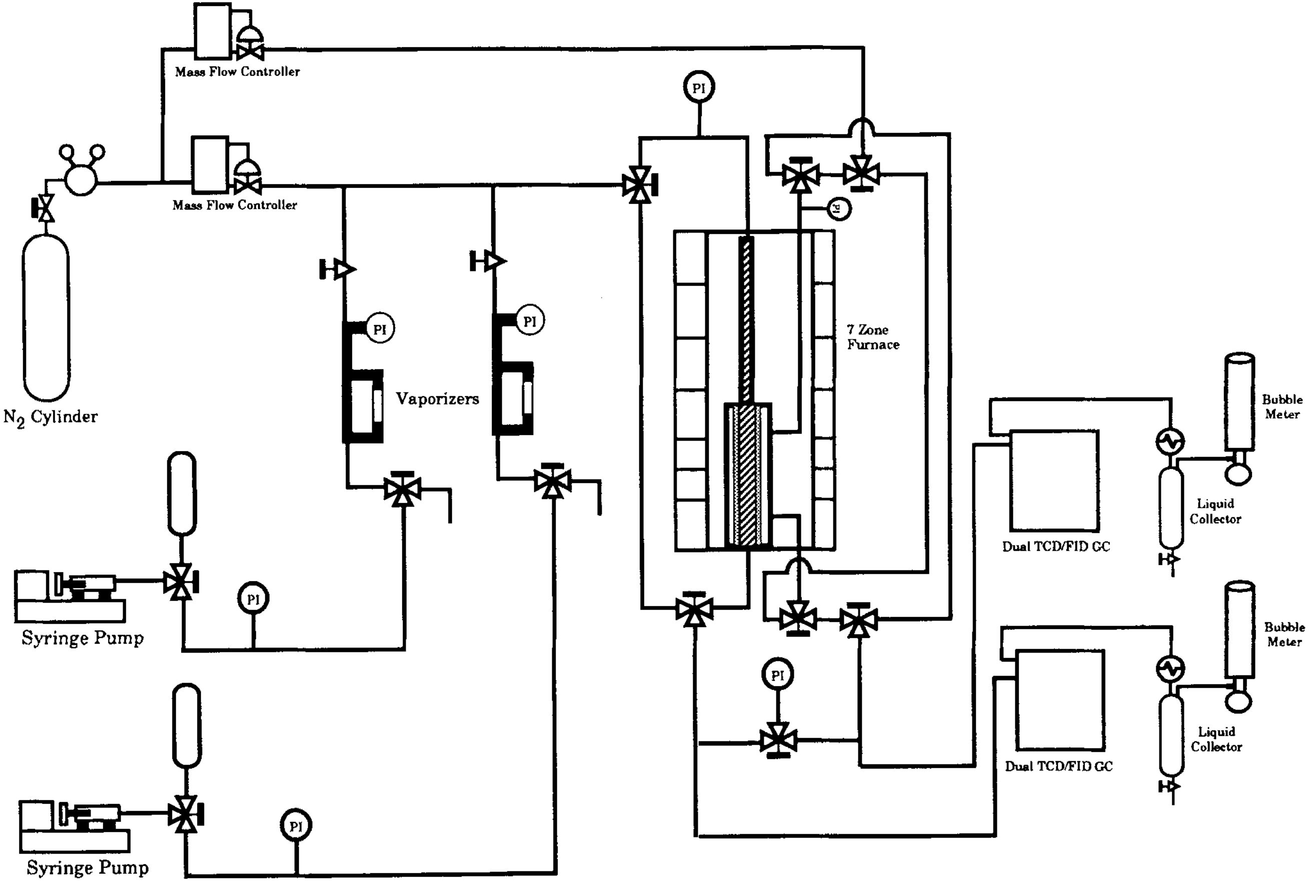

FIGURE 1. Schematic of the reaction system for ethylbenzene dehydrogenation in a ceramic membrane reactor.

the membrane module. High-temperature pressure transducers are located at the inlet and outlet of the reactor to monitor feed, reject, and permeate pressures.

A bypass is installed around the reactor. During startup, the feed flow is diverted around the reactor so that steam and ethylbenzene vapor flows can stabilize. The reactor is heated to temperature at approximately 10°C/minute in flowing N_2. Once the feed flow and reactor temperature stabilize, the feed is switched into the reactor. This procedure protects the catalyst and membrane from the flow fluctuations that can occur during this transient period.

A detailed schematic of the membrane module is shown in Fig. 2. The ceramic membrane is sealed in the stainless steel module via packing glands and graphite ribbon packing. The membrane tube is packed with a commercial, potassium-promoted iron oxide styrene catalyst from United Catalysts. The commercial pellets are crushed and sieved through 14 mesh onto 28 mesh before packing to increase packing density in this benchscale configuration. A four-point thermocouple is placed in the catalyst bed to monitor reaction temperatures at the inlet and outlet of the reactor as well as at points 1/3 and 2/3 of the way along the bed. In addition, three single-point thermocouples are placed along the shell side of the module to monitor permeate temperatures.

Permeate and reject streams exit the furnace and flow to separate dual FID/TCD gas chromatographs for simultaneous online sampling. The analytical protocol uses a Hayesep D column on the TCD side and a Porapak Q column on the FID side. H_2, N_2, CO, CO_2, CH_4, and water are analyzed on the TCD side. The Hayesep D column gives a particularly nice peak for water with no detectable permanent holdup and little peak tailing. Methane, ethylene,

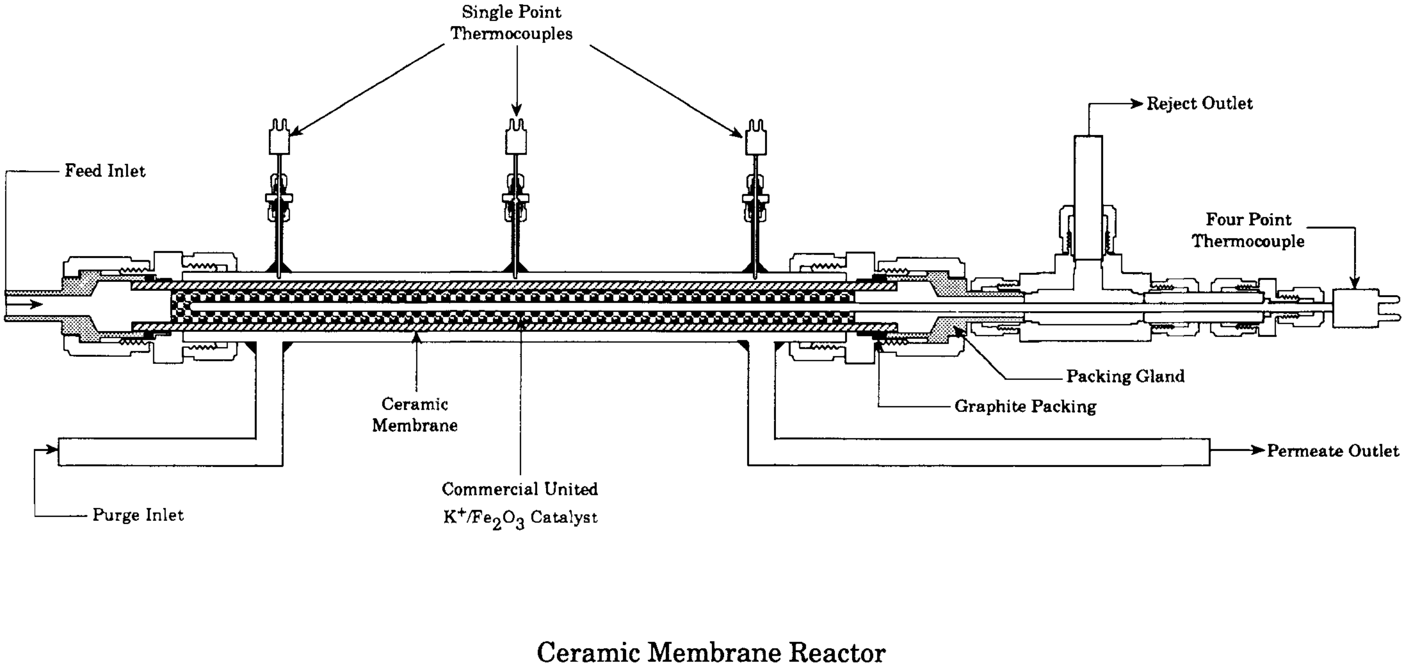

FIGURE 2. Schematic of the ceramic membrane reactor.

TABLE 1. ETHYLBENZENE DEHYDROGENATION INDUSTRIAL OPERATING CONDITIONS

Catalyst	Cr, K/Fe_2O_3
Pressure	≤ 20 psig
Temperature	580°C - 610°C
Temperature Profile	Isothermal, Adiabatic
H_2O/EB	6:1 - 14:1
EB LHSV	0.4hr^{-1} - 0.6 hr^{-1}
Ethylbenzene Conversion	60% - 70%
Styrene Yield	90% - 95%

ethane, benzene, toluene, ethylbenzene, and styrene are analyzed on the FID side. The sample is injected at 40°C. This temperature is held for 2 minutes before ramping at 25°C/min to 245°C followed by another hold period. All products elute within 20 minutes. Total turn-a-round for the analysis is 30 minutes.

The streams exit the gas chromatographics and pass through condensers. The condensable fractions are collected and the gas flow rates are measured with bubble meters before venting to a fume hood.

The membrane utilized in this study was an asymmetric Membralox® (Alcoa), single tube with a nominal 40Å, γ-Al_2O_3 separating layer. The tube has an inner diameter of 7 mm, an outer diameter of 10 mm, and an overall length of 250 mm. Details of the characteristics of this membrane have been reported elsewhere (1,5).

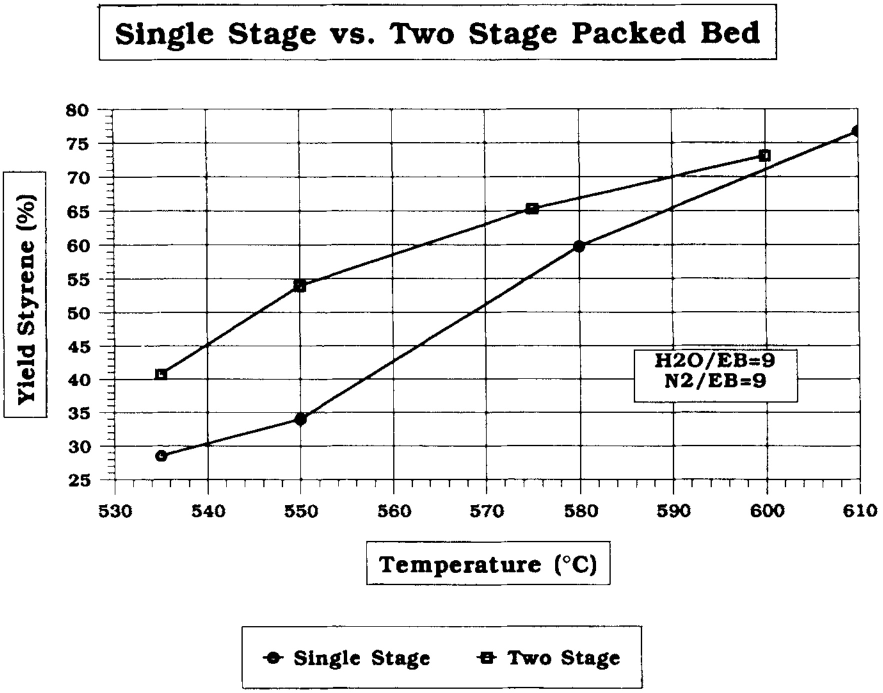

FIGURE 3. Comparison of styrene yield in a single stage packed bed vs. a two stage packed bed as a function of temperature.

REACTION RESULTS

The system described above enables evaluation of ethylbenzene dehydrogenation under realistic industrial conditions. Typical industrial operating conditions are summarized in Table 1. The initial commercialization of membrane reactors for styrene production will likely be as an add-on stage to an existing series of packed-bed reactors. This configuration would minimize capital expense and risk to the end user while adding flexibility to the existing process. With this consideration, experimentation was undertaken to compare the performance of a packed-bed reactor with

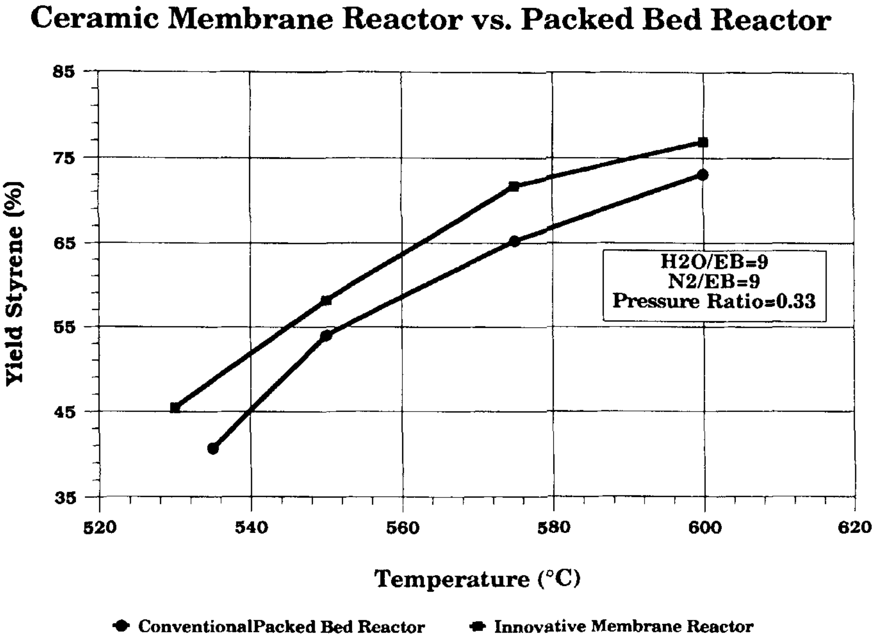

FIGURE 4. Comparison of styrene yield in a hybrid ceramic membrane reactor vs. a two stage packed bed as a function of temperature.

an add-on stage ceramic membrane reactor to that of a packed-bed reactor with an additional packed bed stage.

Single-Stage Packed Bed vs. Two-Stage Packed Bed

In the industrial operation, the discharge from the reactor train is near equilibrium. Adding another packed bed would result in no further styrene production, but side reactions to benzene and toluene would continue since these reactions consume hydrogen. The net result would be a loss of styrene selectivity.

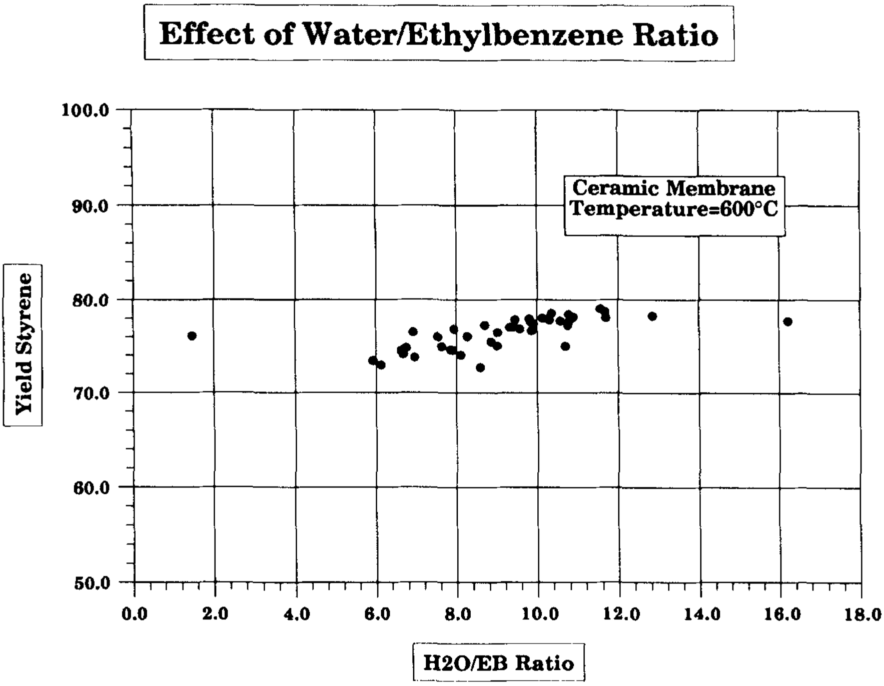

FIGURE 5. Effect of varying molar water to ethylbenzene ratio on styrene yield in a hybrid ceramic membrane reactor at 600°C.

The first study undertaken evaluated the effect of adding an additional packed-bed stage to a single packed-bed reactor. Results of this study are shown in Fig. 3.

The single-stage packed bed was prepared by packing a stainless steel tube mounted in the membrane module with 9.0g of crushed catalyst. The two-stage reactor was assembled by packing an additional 7.5g of catalyst in the module preheater. Flows were set to yield an ethylbenzene LHSV of 0.4 hr^{-1} in the two-stage configuration. The same flow rates were used in the single-stage mode resulting in

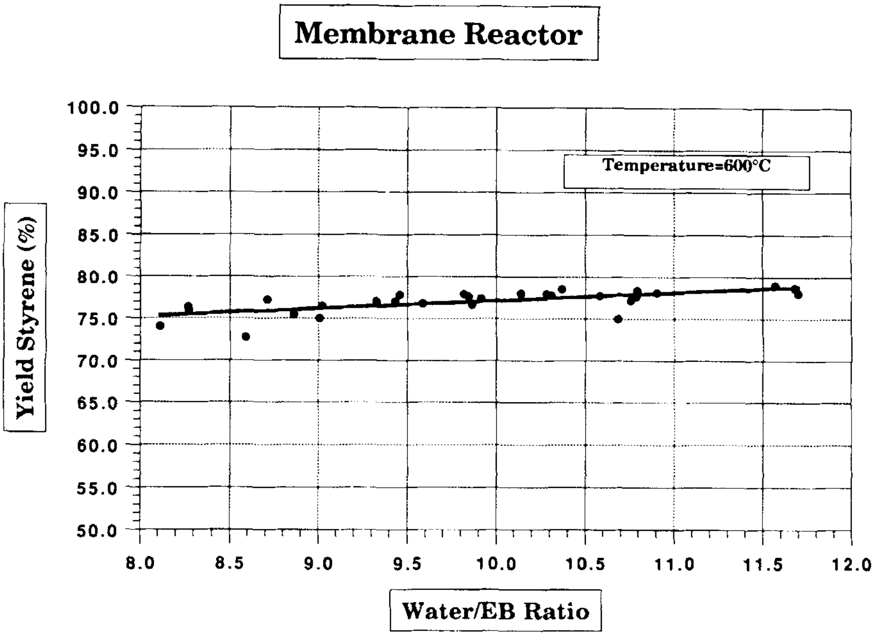

FIGURE 6. Linear regression of styrene yield over a finite range of molar water to ethylbenzene ratio for a hybrid ceramic membrane reactor at 600°C.

an ethylbenzene LHSV of 0.75 hr^{-1}. A water to ethylbenzene molar ratio of 9 was targeted. The N_2 carrier flowrate in the feed was fixed at a 9:1 N_2:ethylbenzene molar ratio. Inlet pressure to the reactor was fixed at 5 psig.

As can be seen in Fig. 3, the two-stage packed bed out performed the single-stage reactor at lower reaction temperatures. However, as reaction temperatures of 600°C were approached, styrene yields from the single-stage and two-stage reactors were nearly identical. This suggests that at the lower temperatures the single-stage reactor was

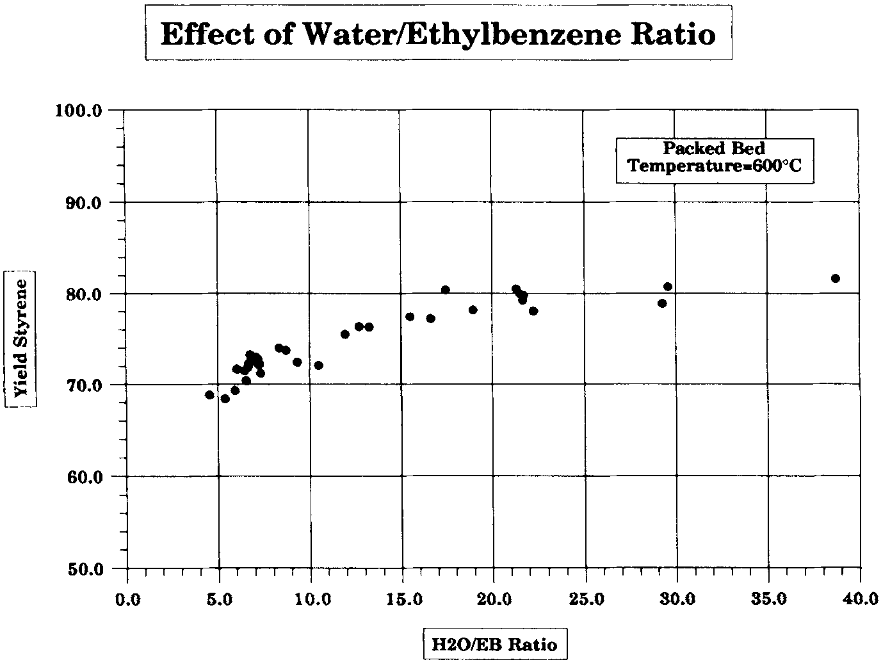

FIGURE 7. Effect of varying molar water to ethylbenzene ratio on styrene yield in a two stage packed bed reactor at 600°C.

not fully equilibrated. This is due to the higher space velocities employed with the single-stage reactor vs. the two-stage reactor. At 600°C the single-stage reactor appears to be fully equilibrated and the addition of a second stage resulted in no further increase of styrene yield.

Two-Stage Packed Bed vs. Packed Bed Ceramic Membrane Hybrid Reactor

The next study compared the performance of a two-stage packed bed with that of a packed bed followed by a ceramic membrane

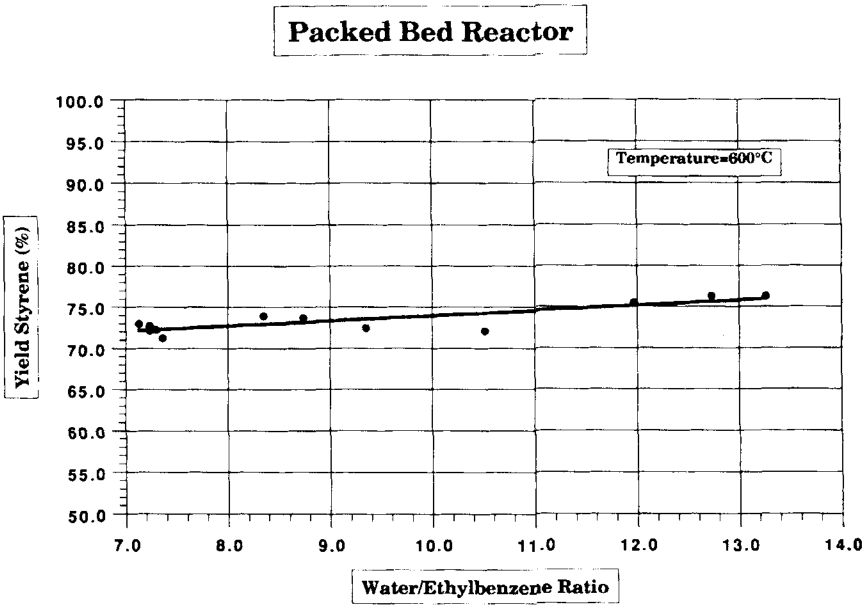

FIGURE 8. Linear regression of styrene yield over a finite range of molar water to ethylbenzene ratio for a two stage packed bed reactor at 600°C.

TABLE 2. CERAMIC MEMBRANE REACTOR VS. PACKED BED REACTOR

	Styrene Yield (%)	
Temperature (°C)	Ceramic Membrane	Packed Bed
530	46	--
535	--	41
550	58	54
575	72	65
600	77	73

TABLE 3. CERAMIC MEMBRANE REACTOR VS. PACKED BED REACTOR

Selectivities

	Temperature (°C)				
	530	535	550	575	600
Styrene					
Membrane	0.98	--	0.96	0.94	0.93
Packed Bed	--	0.98	0.96	0.95	0.93
Benzene					
Membrane	0.01	--	0.02	0.02	0.02
Packed Bed	--	0.01	0.02	0.02	0.03
Toluene					
Membrane	0.01	--	0.03	0.04	0.05
Packed Bed	--	0.01	0.02	0.03	0.04

reactor. The results are summarized in Fig. 4-8 and Tables 2 and 3. The two stage packed bed was configured as described above. For the hybrid reactor, the stainless steel tube in the module was replaced with a 40Å pore size ceramic membrane packed with 9.0g of crushed commercial catalyst. Flows were fixed to yield ethylbenzene LHSVs of 0.4 hr^{-1} for both reactors. Inlet pressures were set at 5 psig resulting in a pressure ratio of 0.33 (average tube side pressure/permeate side pressure) for the membrane reactor.

As shown in Fig 4 and Table 2, the hybrid reactor outperformed the packed-bed reactor at each reaction temperature. Styrene yields were enhanced in the hybrid reactor by about 4% throughout the range of temperatures investigated. Table 3 summarizes data on reaction selectivity for both the packed bed and hybrid reactors. Focusing first on the packed-bed data it can be seen that as expected, increasing yield with increasing reaction temperature resulted in a drop-off of selectivity to styrene. Comparing these results with those from the hybrid reactor, it can be seen that the 4% enhancement in styrene yield in the hybrid reactor comes with no loss in selectivity to styrene.

The results shown in Fig. 4 and Tables 2 and 3 represent a condensation of all the data points taken for each reaction run. The results of a typical run are shown in Fig. 5 for the membrane reactor at 600°C. Despite attempts to carefully control feed flowrates, some variation in the water/ethylbenzene ratio occurs. In analyzing the data, styrene yield is plotted vs. this ratio. Styrene yield increases with water/ethylbenzene ratio then plateaus at values above about 12. This effect is due to a combination of steam reacting with deposited carbon to prevent catalyst deactivation and steam dilution of the reaction mixture thereby shifting the reaction equilibrium. At high ratios, the beneficial effect of lowering H_2 partial pressure is offset by dilution of reactant ethylbenzene partial pressure. The commercial catalyst employed is designed for a water/ethylbenzene ratio of 9-10 which approximates the break point in the curve in Fig. 5. Fig. 6 shows a linear regression of the data over the range of water/ethylbenzene ratios from 8 to 12. Data in this range are well fit by a straight line. The regression equation is then used to determine the styrene yield at a water/ethylbenzene ratio of 10. The variation of styrene yield with water/ethylbenzene ratio and data regression for a run in the packed bed are shown in Fig. 7 and 8 respectively for comparison purposes. The method of data analysis described above was used for all results in Fig. 4 and Tables 2 and 3.

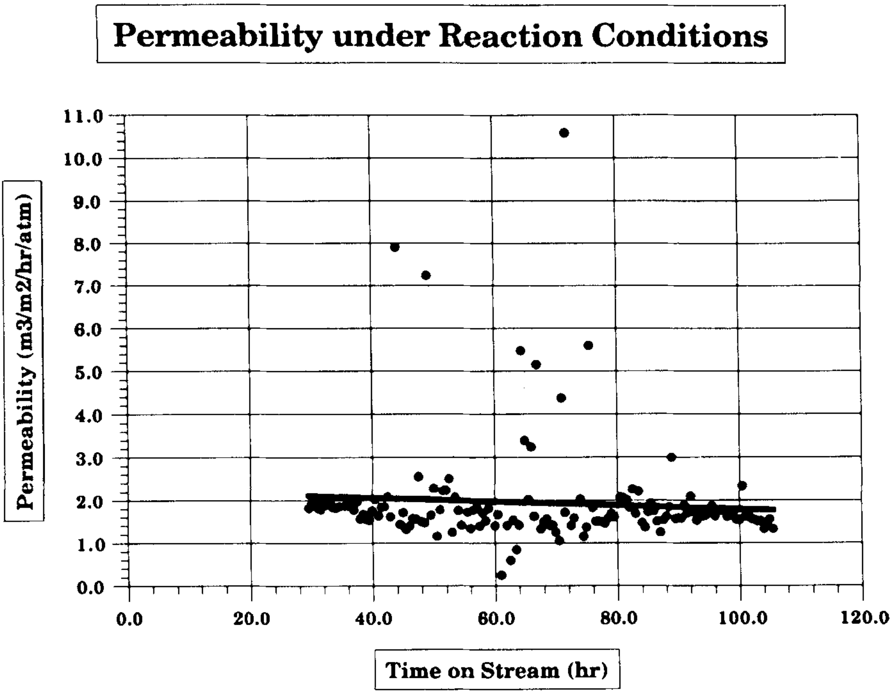

FIGURE 9. Permeability through a ceramic membrane under ethylbenzene dehydrogenation conditions as a function of reactor time on stream.

Membrane Permeability under Reaction Conditions

The dehydrogenation of ethylbenzene to styrene also results in significant carbon deposition on the catalyst necessitating the addition of steam to react with the carbon and prevent catalyst deactivation. For the membrane reactor, the impact of carbon deposition on membrane permeability was an additional concern. Fig. 9 shows the permeability of the membrane as a function of time on stream at a reaction temperature of 600°C.

Characterization studies have shown that the permeability of fresh membranes is typically about 70 $m^3/m^2/hr/atm$. Thermal treatment at 600°C drives off adsorbed moisture and results in an increase of permeability to 110 $m^3/m^2/hr/atm$ without any change in the 40Å nominal pore size (6). As can be seen from Fig. 9, the steady state permeability under reaction conditions is approximately 2 $m^3/m^2/hr/atm$. These permeability values are determined by converting the observed molar flux at reaction temperature to a volumetric flux at STP. This level of permeation suggests that carbon does deposit on the membrane in the initial stages of reaction, but that the presence of steam in the reaction mixture results in a dynamic equilibrium between carbon deposition and removal.

The critical requirement for permeation is that sufficient H_2 flux be present so that the reactor does not re-equilibrate and thereby behave like a packed bed. This appears to be the case here, although this permeability is probably not the optimum. It is possible that a higher H_2 permeability would result in further enhancement of styrene yield. However, reduced permeability can benefit the reactor by preventing bypassing of the catalyst bed by the reactant ethylbenzene. Membrane permeability and pore size distribution after long-term exposure to reaction are targeted for study as part of the optimization of the hybrid reactor.

CONCLUSIONS

A benchscale reactor system capable of experimentally simulating the industrial operation has been developed for the dehydrogenation of ethylbenzene to styrene. Initial results comparing the performance of a hybrid packed bed-ceramic membrane reactor to a traditional two-stage packed bed showed a 4%

improvement in styrene yield in the hybrid reactor. This yield improvement came at no loss in styrene selectivity. During reaction, the permeability of the membrane declined from an initial value of 70 $m^3/m^2/hr/atm$ as a result of carbon deposition on the membrane. After approximately 40 hours of operation, however, a steady state value of 2 $m^3/m^2/hr/atm$ was attained, representing a dynamic balance between carbon deposition from the reaction mixture and carbon removal due to the presence of steam. Future efforts will focus on optimizing the performance of this hybrid reactor.

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