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The catalytic dehydrogenation of isobutane to isobutene in a palladium/silver composite membrane reactor

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Abstract

Isobutane dehydrogenation to isobutene has been investigated experimentally and by modelling for a membrane reactor and a fixed bed reactor under similar operating conditions using a Pt/alumina catalyst. Reaction kinetics were obtained from experiments in the fixed bed reactor. Comparative tests showed that the membrane reactor achieved much higher yields of isobutene and also gave higher selectivities, with less by-products than the fixed bed system.

Using the kinetic data, the simulations gave good agreement with the fixed bed experiments, but over predicted the yields from the membrane reactor. Analysis of these results indicated that in the membrane reactor the hydrogen permeability of the membrane was much greater than its hydrogen transfer requirement and that the reaction rate was the determining factor for isobutene yield.
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Keywords: Isobutane dehydrogenation; Membrane reactors; Simulation

1. Introduction

The demand for olefins and olefinic products continues to increase and commercially has resulted in a number of catalytic dehydrogenation processes. Current processes for propene and butenes production from the corresponding alkanes employ mainly fixed bed operation, but because of the necessarily high temperatures involved in these reversible endothermic reactions, catalyst coking rapidly occurs, so that frequent catalyst regeneration is required. To overcome this problem a number of alternative procedures have been suggested. One of these is oxidative dehydrogenation in which partial oxidation of the alkane limits to some extent the endothermic reaction requirement. A sizeable amount of information on this method is available in the literature especially for propane dehydrogenation [1–4]. A drawback is the potential problem of flammability, with the necessity of adopting a distributed feed in some instances [5].

An alternative is the use of a membrane reactor. In recent years, the possibility of overcoming the equilibrium constraint in reversible reactions such as dehydrogenations has attracted wide attention. Separation of the hydrogen product permits a higher conversion or better selectivity to be achieved. Alternatively, operation may be made under less severe conditions with a consequent reduction in the extent of coking and less need to regenerate the catalyst.

Porous membranes such as glass and alumina [6,7] have been used to study the catalytic dehydrogenation of hydrocarbons and conversions as high as two to seven times the equilibrium level have been observed for some reactions [8–10]. However, these membranes exhibit poor selectivity, due largely to the nature of the flow process in their pore structure.

Dense metallic membranes on the other hand, such as palladium and its alloys possess exclusive selectivity to hydrogen and if they can be made sufficiently thin can provide adequate fluxes for hydrogen [11,12]. The usual method of achieving this is to use a porous metal or ceramic, onto which a very thin but selective film is deposited. Typically such membranes have hydrogen permeabilities of about 10^{-1} mol m^2 s^{-1} bar^{-1} [13,14].

Isobutane dehydrogenation using catalytic membrane reactors has been studied previously by a number of

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researchers. Ionnides and Gavalas [15] used a dense silica membrane reactor and obtained increases in selectivity and yield over a fixed bed reactor at higher space times. Matsuda et al. [16] employed a palladium membrane reactor and tested both a chromia/alumina and a platinum alumina catalyst. The isobutene yield for both was greater than for a conventional reactor. Shu et al. [17] used a membrane reactor with a very thin palladium film, while Casanave et al. used both microporous and zeolite membrane reactors for this reaction [18,19]. Further zeolite membrane reactor results by Ciavarella et al. [20] discussed the effect of operating conditions. Using a palladium membrane reactor, Raybold et al. [21] found that due to the very slow kinetics obtained in their system, it was necessary to add oxygen to the feed to increase the yield of isobutene.

In the present paper, the performance of a palladium/silver membrane reactor containing a platinum catalyst within the membrane tube, is compared with a conventional fixed bed reactor under the same operating conditions. Experimental kinetic data obtained for the Pt/Al_2O_3 catalyst used were employed to develop mathematical models to predict the performance of both the membrane and the fixed bed reactor.

2. Experimental

Experiments were conducted in a membrane reactor comprising a porous stainless steel tube (average pore diameter 1.2 μm) on the outside surface of which a palladium/silver film was coated. Details of the procedure are given elsewhere [22,23]. This composite membrane tube was surrounded by a coaxial heated shell of stainless steel. The effective length of the membrane was 180 mm with an outside diameter of 12.7 mm. Sealing of the membrane tube within the reactor was achieved using graphite rings.

Equant 3 mm pellets of 0.5% Pt/alumina were placed within the bore of the membrane tube. The fixed bed reactor comprised a non-porous stainless steel tube of the same dimensions as the membrane tube and contained the same amount of catalyst. The palladium/silver film was deposited by sequential electroless plating, followed by annealing at 700 °C to give a film of 10 microns thickness with a composition of approximately 20% silver. The resultant Pd/Ag membrane had a hydrogen/nitrogen selectivity of 1200 to 1500 depending on the pressure difference and gave a hydrogen permeance of 0.8 to 1.0 μ mol/(m^2 s Pa).

The feed stream was a mixture of 80% isobutane and 20% hydrogen, fed at isobutane flow rates from 168 to 314 ml/min and both gas steams were mass flow controlled. Nitrogen gas was used as sweep, cocurrent to the reactant feed.

Product analysis was by gas chromatography for the hydrocarbon gases using an FID detector, while a hydrogen gas analyser measured the concentrations of hydrogen on-line at the exits of both shell and tube sides of the membrane reactor. Temperature profiles for both reactors were constant to within 3 °C over the effective length of both reactors.

3. Results and discussion

Initial experiments were made with a commercial chromia/alumina catalyst located within the reactor tube of the fixed bed reactor, but this failed to produce significant yields of isobutene within the temperature range of interest (450–520 °C). Therefore, a platinum/alumina catalyst was used in all subsequent experiments.

The activity of this catalyst was tested in the fixed bed mode and a sharp drop of activity was observed, the conversion of isobutane falling to less than 5% over a period of 6 h. In order to avoid this rapid activity decrease the addition of 20% hydrogen was made to the isobutane feed and the results for both the fixed bed and the membrane reactor are illustrated in Fig. 1 together with the case where no hydrogen was added. Clearly the addition of hydrogen has provided a more stable catalyst activity, although a slow decrease is still observed. However, throughout the period of a measurement (up to 2–3 h) the activity was essentially constant. The activity decrease for the membrane reactor was slightly greater than that for the fixed bed mode even with hydrogen addition; this is due mainly to the removal of hydrogen by permeation from the tube side in the membrane reactor giving a higher concentration of olefin which has a greater potential for coke deposition than the isobutane.

All reported experiments for the membrane reactor were made with a sweep gas of nitrogen at flow rates from 100 to 1000 ml/min and atmospheric pressure on the sweep side. In addition, a fairly high flow rate of 168 ml/min of isobutane combined with 42 ml/min of hydrogen was adopted in most experiments. Since the catalyst particles used had the platinum deposited on the external surface, intraparticle concentration gradients were absent. Estimates [24] of the partial pressure difference of the reactant isobutane between

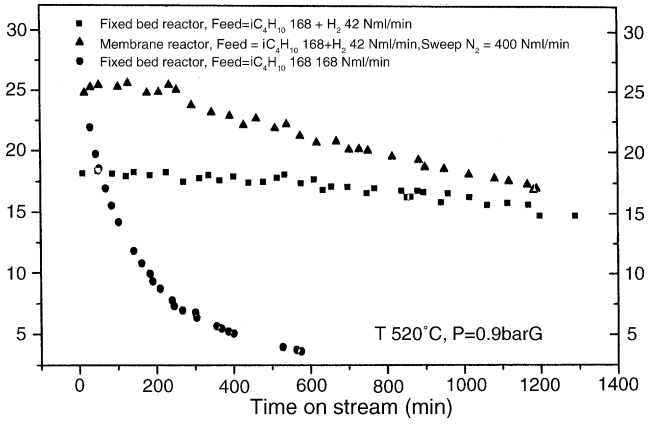

Fig. 1. Conversion of i-C_4H_{10} vs. time on stream. Effect of hydrogen addition.

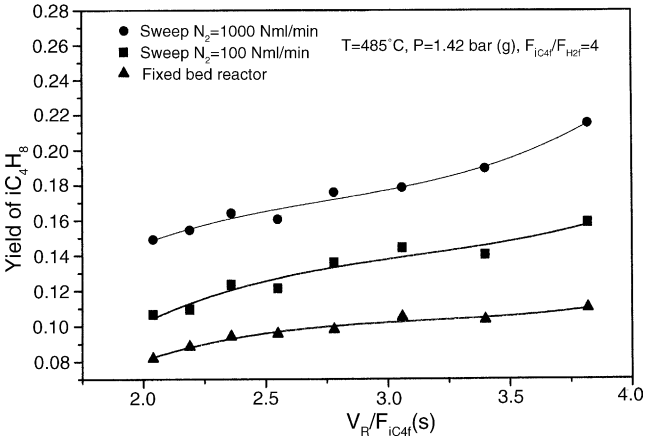

Fig. 2. Yield of i-C_4H_8 vs. residence time (P = 1.42 bar, T = 485 °C).

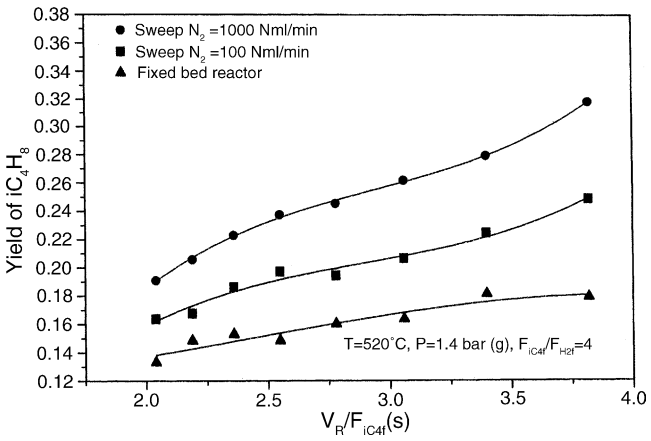

Fig. 3. Yield of i-C_4H_8 vs. residence time (P = 1.4 bar, T =520 °C).

the bulk gas and the surface gave values of less than 0.5% indicating that the flow rate used was sufficient to overcome any external mass transfer restriction. Also, because the platinum in the platinum/alumina catalyst pellets was deposited solely on the outer surface of the catalyst pellets, internal diffusion of reactants and products within the catalyst pellet can be neglected. Hence, under the experimental conditions used in the present work neither form of mass transfer was important.

The effect of sweep gas flow rate is shown in Figs. 2 and 3 for temperatures of 485 and 520 °C, respectively, where yields of isobutene are plotted against residence time for the fixed bed reactor and for the membrane reactor with two sweep flow rates of 100 and 1000 ml/min. The yield of isobutene increased slowly as the residence time increased, but the major effect was the increased yield shown by the membrane reactor compared with the fixed bed reactor. Thus, for a temperature of 485 °C (Fig. 2) at a residence time of 3.5 s the yield for the fixed bed reactor was 10%, that for the 100 ml/min sweep was 15% and for the 1000 ml/min sweep a value of 20% was attained. Fig. 3 shows the corresponding plots at the higher temperature of 520 °C. The yield increases with residence time as for the lower temperature, but the yields of isobutene are significantly higher with 17% attained for the fixed bed reactor and 22 and 29% for the 100 and 1000 ml/min sweep flows in the membrane reactor, all at a residence time of 3.5 s.

Equilibrium yields calculated from the feed conditions used were 11.6 and 20.7 for temperatures of 485 and 520 °C, respectively. For the fixed bed reactor in Fig. 2 the equilibrium yield is barely attained even for the highest residence time of 3.7 s. However, use of a sweep gas with the membrane reactor, enables the equilibrium yield to be exceeded for all residence times and at a sweep flow of 1000 ml/min and a residence time of 3.7 s the experimental yield is almost double the equilibrium value.

Similar results are obtained at 520 °C (Fig. 3), but now the equilibrium yield of 20.7% is exceeded throughout the whole range of residence times for the highest sweep rate only. Clearly the increased equilibrium yield is not matched by a corresponding increase in the hydrogen permeation rate.

The product stream from the membrane reactor was found to consist of isobutane, isobutene, hydrogen, methane, propane/propene and very small amounts of C2 and C4 hydrocarbons. This result is consistent with previous reports [15,17,19] and the main side reaction is assumed to be either isobutane decomposition

$$i - C_4H_{10} \rightarrow CH_4 + C_3H_6$$

but it seems more likely in the present context that the hydrogenolysis reaction

$$i - C_4H_{10} + H_2 \rightarrow C_3H_8 + CH_4$$

is predominant, because the equilibrium constant of the former reaction is very small under the present operating conditions.

The fractional conversion to by-products is illustrated in Fig. 4 for an operating temperature of 520 °C for two membrane reactor sweep flow rates and for the fixed bed (conventional) reactor. The fixed bed reactor shows a three-

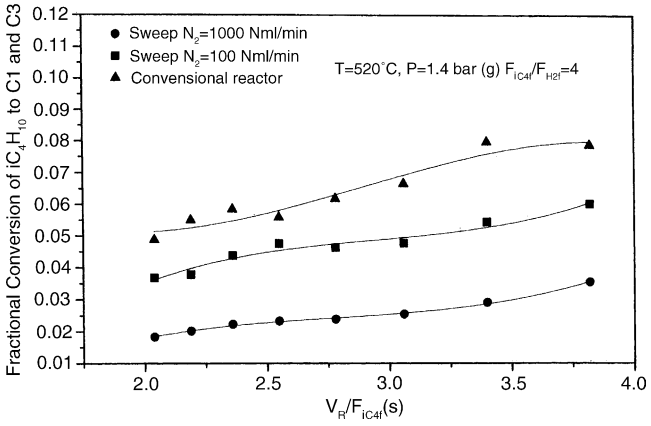

Fig. 4. Conversion of i-C_4H_{10} to by-products vs. residence time (P = 1.4 bar, T = 520 °C).

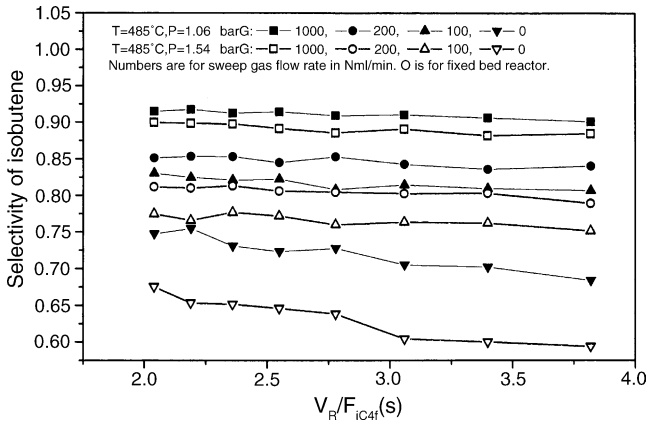

Fig. 5. Selectivity comparison between two pressures ($T = 485$ °C).

fold increase in by-products compared to the membrane reactor with the higher sweep rate.

The higher yields obtained with the membrane reactor with a sweep gas are caused in part by the higher selectivities compared to fixed bed operation as shown in Fig. 5 for two bed pressures of 1.06 and 1.54 bar. In general, a lower pressure favours selectivity since a lower pressure is beneficial for the main reaction which occurs with a volume expansion, but should have no effect on the side reaction. This was observed in the fixed bed reactor where for the shortest residence time of 2 s a selectivity of 75% at 1.06 bar and 67% at 1.54 bar was obtained whereas the membrane reactor showed a progressive narrowing of the yield difference between the two pressures as the sweep flow increased until at a sweep flow of 1000 ml/min the difference was only 1–2%. Furthermore, all membrane reactor selectivities were greater than those for the fixed bed, lying in the range from 75 to 92%. Another feature is that the selectivity of the fixed bed reactor decreased with increase in residence time as might be expected, due to increase of side reactions with a longer residence of reactants and products in the catalyst bed. No such behaviour was observed for the membrane reactor, where the selectivity was almost entirely independent of residence time.

The increased conversion in the membrane reactor with increase of pressure is due primarily due to hydrogen removal from the reaction zone, so that the dehydrogenation reaction occurred in a region remote from equilibrium. Also higher pressure is more favourable for hydrogen removal from the membrane. However, selectivity is a result of the different rates of the main and side reactions. A higher operating pressure increases the rate of the reverse of the main reaction and hence slows down the main forward rate, but the side reaction is unaffected. Therefore, the selectivity becomes lower as the pressure is increased. Nevertheless, a high sweep flow rate removes more hydrogen, resulting in a lower hydrogen partial pressure, which reduces the rate of the reverse of the main reaction and also reduces the rate of the side reaction. As mentioned above, high pressure facilitates the membrane's removal of hydrogen and consequently the effect of pressure on selectivity becomes less.

3.1. Simulation

The simulation of the fixed bed reactor is based on the following assumptions:

- flow within the reactor tube is in plug flow;
- operation is isothermal and isobaric.

For the simulation of the membrane reactor, in addition to the above assumptions the following conditions were also applied:

- the membrane is permeable to hydrogen only;
- the sweep gas is also in plug flow;
- diffusion of hydrogen through the Pd/Ag membrane is in accordance with the relation $J = K[(P_{Hf})^n - (P_{Hs})^n]$, where K and n are constant at a given temperature and are obtained from permeation measurements. The subscripts Hf and Hs refer to hydrogen partial pressures on the feed and shell sides of the membrane, respectively.

Regression analysis of the conversion–residence time data from the fixed bed reactor were used to derive rate expressions for both the main and side (hydrogenolysis) reactions. The appropriate rate equations were:

At 485 °C

$$r_{A1} = 2.106\left(P_A - \frac{P_B P_C}{0.0782}\right)$$

$$r_{A2} = 0.989 P_A P_B$$

At 520 °C

$$r_{A1} = 2.462\left(P_A - \frac{P_B P_C}{0.196}\right)$$

$$r_{A2} = 1.212 P_A P_C$$

where r_{A1} and r_{A2} refer to the dehydrogenation and hydrogenolysis reactions, respectively and the subscripts A, B, and C represent in turn isobutane, isobutene and hydrogen.

These reaction rate equations were incorporated into the model.

Good agreement was obtained between experimental and simulation results for the fixed bed reactor. However, the simulation results for the membrane reactor gave consistently slightly higher values than those for experiments. A typical plot is shown in Fig. 6 and although there is appreciable scatter in the experimental values the difference is apparent especially for the higher sweep rates. Permeation measurements had shown a decline in hydrogen perme-

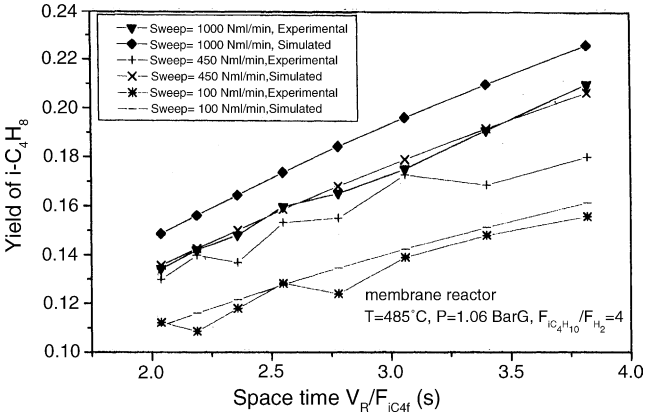

Fig. 6. Comparison of the yield of i-C_4H_8 between experimental and simulated results.

ability after the first few experiments, which was attributed to contamination from feed and product gases. Hence, it is believed that the hydrogen permeabilities in the membrane reactor are lower than those for the fresh membrane, the latter being the values taken for the simulations such as that shown in Fig. 6. Empirically, it was found that if the hydrogen permeability was reduced to about 20% of the value obtained from the hydrogen permeation measurements, where an uncontaminated membrane was used, the simulated results for the membrane reactor are now consistent with their experimental counterparts as shown in Fig. 7. In this figure, the fractional values of the original (measured) permeablities are denoted by the symbol f.

A comparison of the simulated yields of isobutene for values of f from 0.21 to 2 for a sweep flow of 600 ml/min is given in Fig. 8, which also shows the fixed bed experimental results for the same operating conditions. It can be noted that the simulated yield of isobutene for an f value of 1 is not much higher than that for $f = 0.21$, and there is barely any difference between the yields for $f = 1$ and 2. This signifies, that in the present research the permeation ability of the

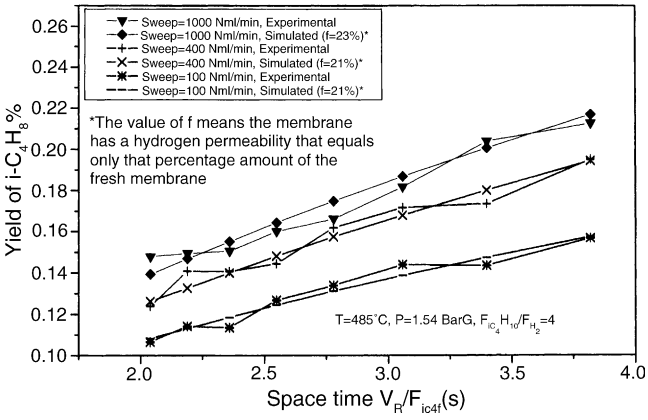

Fig. 7. Yield comparisons between experiment and simulation for f-values of approximately 0.2.

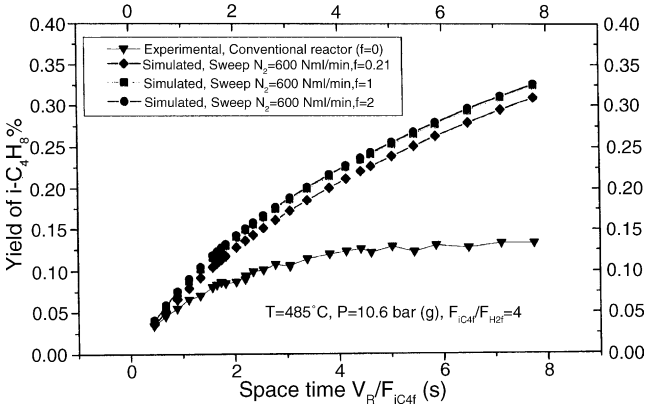

Fig. 8. Effect of varying hydrogen permeability on the yield of isobutene.

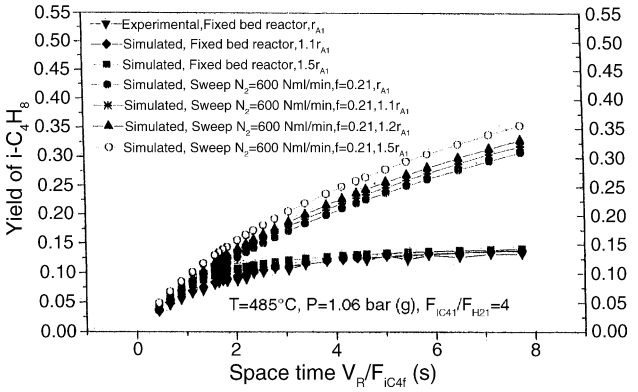

Fig. 9. Effect of reaction rate on the yield of isobutene.

membrane is not limiting. It is the reaction kinetics that limit the yield of isobutene.

Confirmation of this is given in Fig. 9, where simulations have been made of isobutene yield versus space time for three assumed reaction rates, based on multiples of the measured experimental reaction rate, r_{A1}. Thus, $1.1r_{A1}$ represents a rate 1.1 times the reaction rate of r_{A1}, while $1.2r_{A1}$ represents a reaction rate 1.2 times faster and so on. For the fixed bed reactor, it is understandable that a higher reaction rate does not affect the yield at high space times because the reaction is reversible. However, in the membrane reactor, the yield of isobutene continues to increase as the reaction rate is increased.

4. Conclusions

A comparison has been made between experimental results obtained for a Pd/Ag composite membrane reactor and a fixed bed reactor for the catalytic dehydrogenation of isobutane to isobutene using a Pt/alumina catalyst. Because of deactivation of the Pt catalyst, experiments were conducted with a reactant feed of 20% hydrogen in isobutane. Two reactions were identified as occurring, the main dehydrogenation reaction and a side reaction produ-

cing C3 hydrocarbons and methane only. Isobutane yields were much higher in the membrane reactor and the higher selectivities obtained with the membrane reactor were the result of the high hydrogen removal rates caused by the sweep gas flow.

Whereas increase of pressure reduced the yield in the fixed bed reactor, the yield increased slightly with pressure in the membrane reactor, confirming that the overall reaction in the membrane reactor was not influenced by equilibrium.

Sweep flow rate plays an important role in increasing the conversion in the membrane reactor, a 10-fold increase in sweep rate producing a conversion increase of between 45 and 55%.

A simple isothermal model of the process was developed, which although giving good agreement with the fixed bed results, indicated that transport in the membrane reactor was not limited by the permeability of the membrane to hydrogen, but was caused by the relatively low values of the reaction rate produced by the catalyst.

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