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Isobutane dehydrogenation reaction in a packed bed catalytic membrane reactor

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A packed-bed catalytic ceramic membrane reactor (PBCMR) was used for the isobutane dehydrogenation reaction. The experimental results have shown that through the use of the membrane reactor one can attain better conversions and yields than in a conventional reactor operating under the same outlet pressure and temperature, and feed composition conditions.

Keywords: Isobutane dehydrogenation reaction; catalytic ceramic membrane reactor

1. Introduction

The membrane reactor concept is not new, for recent reviews see refs. [1,2]. Its origins go back to the late fifties. It is a rather simple concept, especially as it applies to equilibrium limited reactions. For a reaction that takes place in a flow reactor, like a plug flow reactor, which has solid impermeable walls, the maximum possible conversion is determined by equilibrium considerations. The conversion can never exceed the equilibrium conversion calculated based on the outlet pressure and temperature conditions and the composition at the inlet. Membrane reactors, on the other hand, have semipermeable walls, which allow one (or more) of the reaction products to leak out of the reactor, while acting (ideally) as solid barriers for the reactants. A driving potential for the reaction to occur is, thus, always maintained since the rate of the reverse reaction never becomes equal to the rate of the forward reaction. One would then expect to get (and in practice often does) complete conversion, even under conditions for which the corresponding equilibrium conversion is small.

The membrane reactor concept is today finding commercial uses, primarily in low temperature applications, in the field of bioengineering for the production of a number of specialty chemicals. The membrane bioreactors typically use polymeric

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membranes, which are not generally thermally resistant to temperatures above 100°C. A concise review of membrane bioreactors has been recently published [3].

Though membrane reactors have been tried, since the beginning, for high temperature catalytic applications, they have yet to realize a comparable degree of commercial success. The earlier applications involved Pd membranes. Pd, together with a limited number of other metals, is unique in the sense that it allows hydrogen to permeate through, while being virtually impermeable to other gases and vapors. The early pioneering research with Pd membranes was done by Gryaznov and co-workers of the former Soviet Union. Their work is impressive, and has recently been reviewed [4]. Gryaznov and co-workers studied many hydrogenation and dehydrogenation reactions and realized considerable success. Pd membrane reactors have yet to find commercial application, however. The problem lies with the mechanical and thermal properties of these membranes. These membranes are reported to become brittle during thermal cycling in a hydrogen atmosphere. They also have low hydrogen permeabilities and are easily poisoned by sulfur and deactivated by coke. Efforts are currently under way by several groups to deal with some of these problems. These efforts involve the development of composite ceramic/metal membranes, microporous Pd membranes and replacing Pd with other metal membranes, like Pt, which are more resistant to poisoning.

Nonporous oxygen conducting membranes have also found frequent use in catalytic membrane reactor applications. The earlier applications involved the decomposition of various oxygen containing compounds like CO, CO_2, H_2O and NO. More recent applications involve various partial oxidation reactions including direct methane activation to produce C_{2+} hydrocarbons (for a recent review see ref. [5]). Microporous Vycor glass membranes have also been used in some of the earlier applications involving the decomposition of H_2S and HI. Other efforts have involved the study of cyclohexane dehydrogenation and the oxidative dehydrogenation of methanol. More recent applications with microporous membranes have involved the use of membranes made by sol–gel techniques, most notably composite γ-Al_2O_3/α-Al_2O_3 tubular membranes. Reactions studied involve ethane, ethylbenzene, butane, propane and methanol dehydrogenation, methane steam reforming and the water–gas shift reaction.

Our group has been involved with the study of catalytic membrane reactors for a number of years. The primary focus of our studies has been on the development of effective design methodologies for designing such reactors. The effort has involved the formulation of mathematical models, which have been tested with experiments in catalytic membrane reactors with the ethane dehydrogenation reaction [6]. Two other reactions have also been studied by our group: propane dehydrogenation to propylene [7] and the methane steam reforming reaction [8] for the production of hydrogen for use in chemically recuperated gas turbines.

In this paper we present preliminary results of an experimental study of the isobutane dehydrogenation reaction in a catalytic membrane reactor.

2. Experimental apparatus and general discussion

Isobutane dehydrogenation to produce isobutylene is becoming, today, an important reaction, since isobutylene is used in the production of MTBE, an important gasoline additive. Isobutylene has so far, primarily, been produced as a by-product of pyrolysis/cracking furnaces. Though catalytic dehydrogenation processes have been around for quite a while, and for obvious reasons there has been added interest in them recently, they have yet to play a dominant role in the overall isobutylene production picture. The problem with the catalytic processes results from the thermodynamics and kinetics of the isobutane dehydrogenation reaction. To attain reasonable yields one must work at higher temperatures. At these temperatures the catalyst undergoes rapid deactivation, and this in turn necessitates the use of frequent catalyst regeneration and significantly complicates process/reactor design. Membrane reactor technology offers a promise here. If, through the use of such reactors, one could attain significant gains in conversion at lower temperatures, one could then conceivably avoid catalyst deactivation and, therefore, the need for frequent catalyst regeneration.

We present here results of our experimental studies of the isobutane dehydrogenation reaction in a catalytic membrane reactor. These studies have shown that it is feasible to attain improvements in yield and even overcome equilibrium yield limitations for this reaction by using a membrane reactor. The experimental system used in our isobutane dehydrogenation experiments is basically the same as the ethane dehydrogenation apparatus described in greater detail elsewhere [9]. It consists of the reactant gas delivery and flow measurement systems, the high temperature catalytic membrane reactor and the product collection and measurement devices. The membrane used was a composite sol–gel alumina membrane with i.d. of 0.7 cm and o.d. of 1.0 cm and a length of 25 cm available commercially under the tradename Membralox^{TM}. It consists of three layers with average pore diameters of 40, 2000 and 8000 Å on the top of a macroporous layer with an average pore diameter of 15 μm. The membrane was wet impregnated [10]. An aqueous solution of CrO_3 was prepared by dissolving an amount of CrO_3 corresponding to 50% of the weight of the top three membrane layers together with an amount of NaOH corresponding to 2 wt%. This solution was then sprayed uniformly on the inner surface of the membrane tube. The tube was then placed in a furnace and dried for 2 h at a temperature of 120°C in flowing synthetic air. After drying, the oven temperature was then increased to 650°C and the membrane was kept for another 2 h. The temperature was then again increased to 760°C. The membrane was kept at this temperature for an additional 4 h. Subsequently, the membrane was let to cool down to room temperature in flowing nitrogen. The whole treatment lasts about 12 h.

The impregnated ceramic membrane was then placed inside the membrane reactor and treated at 650°C in flowing hydrogen. The membrane reactor consists of a stainless steel tube with ports corresponding to the membrane inlet and outlet, the

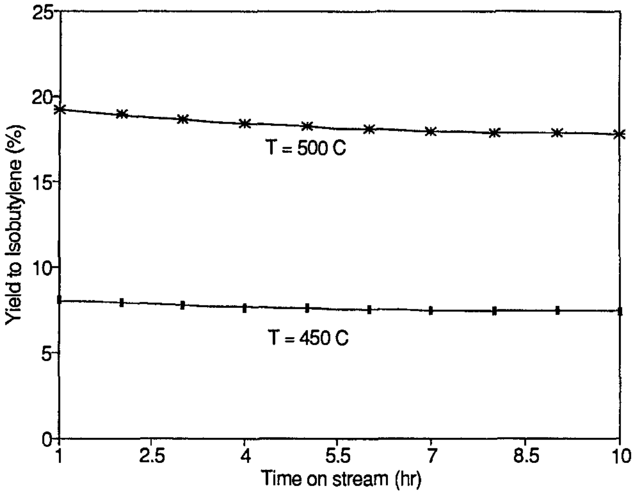

Fig. 1. Yield to isobutylene versus time on stream.

sweep gas inlet and outlet, and to the various thermocouple wells. The inorganic membrane is sealed inside the reactor using graphite string and compression fittings. Heating for the reactor is provided by six semicylindrical heaters (Fisher) connected to three temperature controllers. A preheating section exists in front of the reactor using another temperature controller. For the experiments reported here the reactor was operated under reasonably isothermal conditions with temperature gradients along the reactor length of less than 2°C.

For the packed bed catalytic membrane reactor (PBCMR) experiments reported here the internal membrane reactor volume (8.5 cm^3) was filled with 4.9 g of 14–18 mesh commercial 11 wt% $Cr_2O_3 + 6$ wt% $K_2CO_3/\alpha\text{-}Al_2O_3$ catalyst (Johnson Matthey Electronics). The reactant mixture fed in the tubeside always consisted of isobutane and hydrogen at a molar ratio $i\text{-}C_4H_{10} : H_2$ equal to 1 : 0.2. The experiments reported here were carried out at two different temperatures, i.e. 450 and 500°C. At these temperatures the catalyst undergoes relatively slow deactivation as can be seen in fig. 1. In this figure we report the yield to isobutylene as a function of catalyst time on stream in the membrane reactor. For these experiments the reactor was operated as a conventional packed-bed reactor with the shellside inlet and outlet closed. Reactor conversion and yield to isobutylene are defined as follows:

$$\text{conversion} = \frac{(\text{mol/s } i\text{-}C_4H_{10})^{\text{in}}_{\text{tube+shell}} - (\text{mol/s } i\text{-}C_4H_{10})^{\text{out}}_{\text{tube+shell}}}{(\text{mol/s } i\text{-}C_4H_{10})^{\text{in}}_{\text{tube+shell}}} \times 100\% , \tag{1}$$

$$\text{yield to isobutylene} = \frac{(\text{mol/s } i\text{-}C_4H_8)^{\text{out}}_{\text{tube+shell}}}{(\text{mol/s } i\text{-}C_4H_{10})^{\text{in}}_{\text{tube+shell}}} \times 100\% . \tag{2}$$

Before the initiation of each series of experiments shown in fig. 1 the catalyst is treated at 500°C overnight in flowing synthetic air and then in flowing hydrogen at the same temperature for 2 h. For the run at 450°C there is a 8.7% relative decline in isobutylene yield over the 10 h experiment. For the 500°C experiment the decline in yield over the same time period is 7.4%. The catalyst could be regenerated completely by the overnight treatment described above. Though the decline in activity is relatively small, care was exercised to collect the data within as short a time from the initiation of the experiment as it was possible. At the end of the series of experiments reported in this paper an experiment was carried out to test the reactivity of the reactor wall. The membrane and the catalyst bed were removed and then the empty reactor underwent the same overnight treatment described above. At 500°C (all thermocouples previously monitoring the membrane surface temperature and the bed temperature were left inside the reactor and they all registered 500 ± 1°C) the conversion was 2.15% and the selectivity 68%, i.e. the yield was 1.46%. For a typical run, after the overnight treatment described above, we would start in the morning by setting up the temperature of operation (for the 450°C experiments) in flowing hydrogen. It would take approximately 1 h for the temperature to stabilize. After the temperature reached steady-state, the reactant mixture would be fed in the tubeside inlet. The reaction would then be allowed to run for 1 h, and then samples were taken from the tubeside and shellside outlets and analyzed by gas chromatography. The measurements would then be repeated every 30 min, the whole membrane reaction run lasting approximately 4 h. The membrane reactor would then be heated to 500°C and the catalyst regeneration procedure (see above) would be repeated. During all experiments reported here the pressure range in the tubeside was 2.3–2.7 psig and in the shellside 0–0.2 psig.

3. Experimental results and discussion

Our goal in the series of experiments reported here was to investigate the isobutane dehydrogenation reaction in a packed bed catalytic membrane reactor and compare its behavior with that of the conventional tubular reactor. We have also studied the effect of two reactor operating variables, namely the reactor residence time and the ratio of the sweep gas flow rate (argon gas in our experiments), to that of the isobutane flow rate in the membrane tubeside. We have also carried out a series of experiments, in which the argon sweep gas was replaced by an isobutane + argon mixture (at a molar ratio of 1 : 0.2). The idea of using a reactant stream as sweep gas was originally suggested by Lund [11].

Fig. 2 shows the effect on reactor behavior (at 450°C) of changing the reactor residence time, while keeping the other parameters constant. The residence time is calculated as (L/V), L being the length of the membrane reactor and V the superficial reactor inlet gas velocity, calculated in terms of overall internal membrane cross sectional area. What we plot in fig. 2 is yield to isobutylene for both the con-

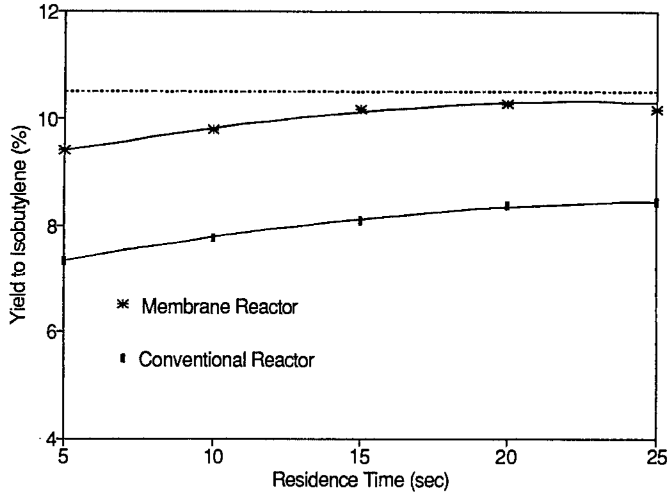

Fig. 2. Yield to isobutylene versus reactor residence time, $T = 450°C$.

ventional and the membrane reactors. The experiments in fig. 2 are in the absence of sweep gas. For comparison purposes the equilibrium yield, corresponding to the outlet temperature and pressure and inlet composition conditions, assuming isobutylene as the only product of the isobutane dehydrogenation reaction, is also shown on the figure (as the horizontal straight line).

Note that as expected, the membrane reactor performs better than the conventional reactor. As the residence time increases the yield for both reactors increases approaching for the membrane reactor the ideal equilibrium yield. Fig. 3 shows the overall conversion and selectivity (defined as the ratio of yield to conversion) to isobutylene for both reactors. Note that as residence time increases, the conversion

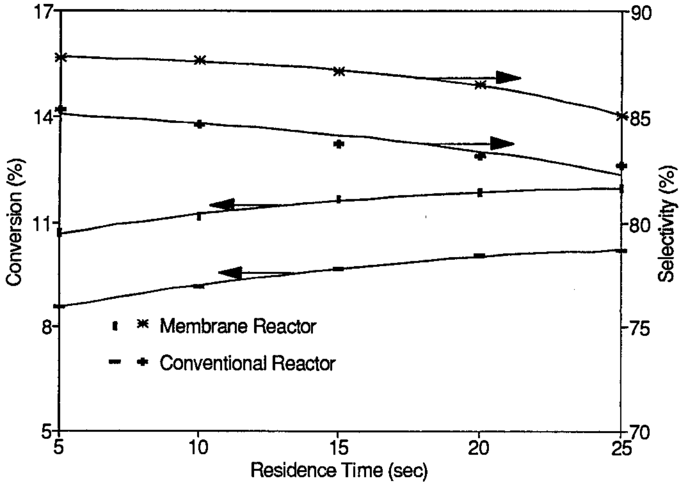

Fig. 3. Conversion and isobutylene selectivity versus reactor residence time, $T = 450°C$.

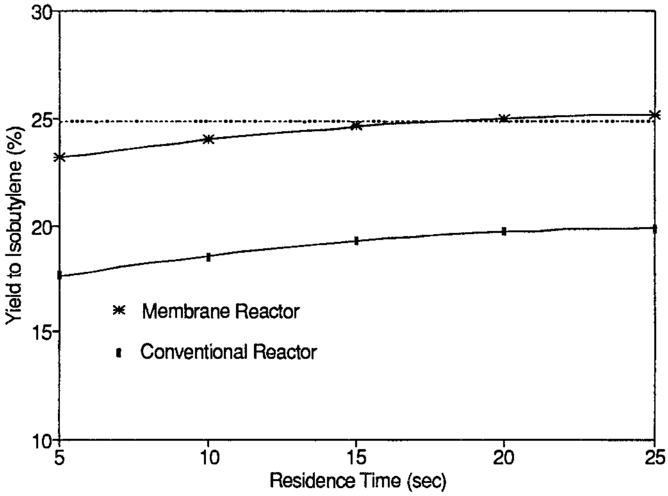

Fig. 4. Yield to isobutylene versus reactor residence time, $T = 500°C$.

increases but selectivity decreases. The conversion of the membrane reactor is higher than that of the conventional reactor. One, furthermore, observes a small but statistically, significant improvement in selectivity. Similar behavior has been observed with the propane dehydrogenation reaction [7]. Figs. 4 and 5 show similar experimental data obtained at 500°C. The behavior is generally the same but the gains in conversion for the membrane reactor are larger.

Fig. 6 shows the effects on reactor behavior of changing the sweep ratio at 450°C (i.e. the ratio of the flow rate of argon, which is used as sweep gas, to the flow rate of isobutane in the inlet of the feedside). What is plotted in fig. 6 is the overall conversion, selectivity and yield to isobutylene. Note that as the sweep ratio

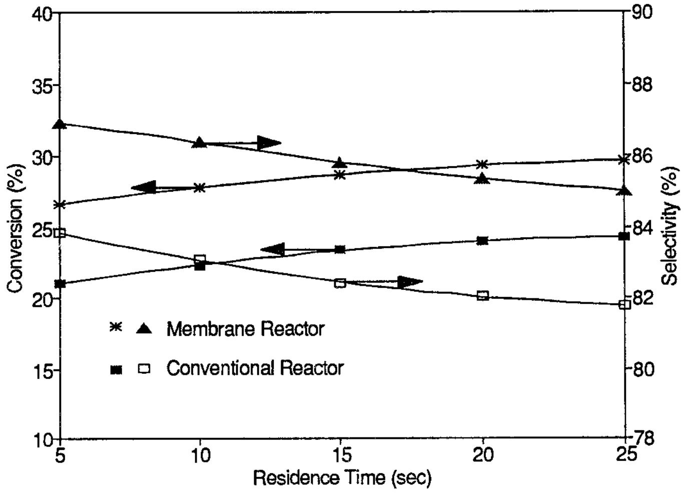

Fig. 5. Conversion and isobutylene selectivity versus reactor residence time, $T = 500°C$.

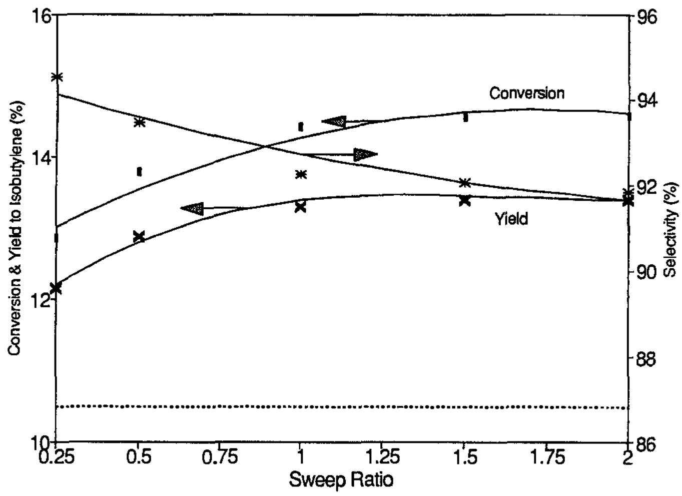

Fig. 6. Conversion, isobutylene selectivity and yield to isobutylene versus sweep ratio, $T = 450°\mathrm{C}$, tubeside reactor residence time = 15 s.

increases both yield and overall conversion increase with the yield exceeding the ideal equilibrium yield of 10.5%. Fig. 7 shows the effects on reactor behavior of changing the sweep ratio at 500°C. Part of the improvement in yield is due to the fact that the sweep gas lowers the concentration of the hydrogen gas in the shellside and, therefore, increases the hydrogen diffusion across the membrane. Part of it, however, is also due to the fact that argon gas back diffuses into the feedside and acts as a dilutant.

Lund [11] recently suggested that for the methane partial oxidation reaction, carried out in a membrane reactor, additional improvements in conversion over the

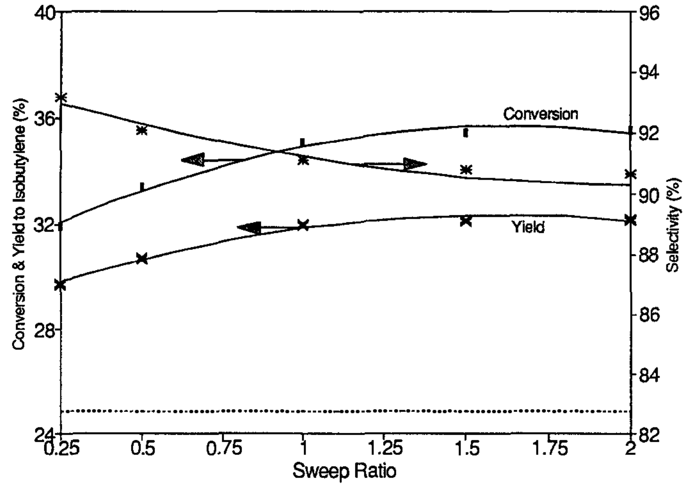

Fig. 7. Conversion, isobutylene selectivity and yield to isobutylene versus sweep ratio, $T = 500°\mathrm{C}$, tubeside reactor residence time = 15 s.

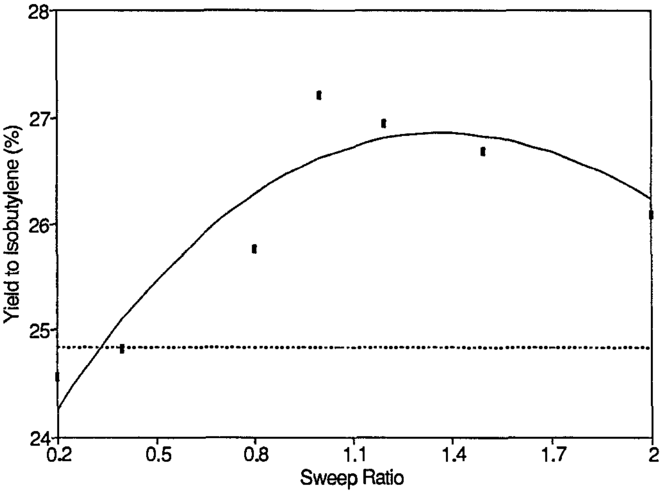

Fig. 8. Yield to isobutylene versus sweep ratio for the reactant swept membrane reactor, $T = 500°C$, tubeside reactor residence time = 15 s.

inert sweep gas case could be attained by using a reactant mixture as the sweep gas. A similar concept had also previously been suggested by Andris et al. [12] for the methane steam reforming reaction. In our experiments, we replaced the argon sweep gas in the shellside by a mixture containing isobutane and argon at a molar ratio of $i\text{-}C_4H_{10}$: Ar equal to 1 : 0.2. The sweep ratio is now defined as the flow rate of isobutane in the shellside to that of isobutane in the tubeside. Fig. 8 shows the effect of sweep ratio on reactor behavior for the reactant swept membrane reactor at 500°C. In this figure we report the yield to isobutylene as a function of the sweep ratio. For comparison purposes a corresponding series of experiments has also

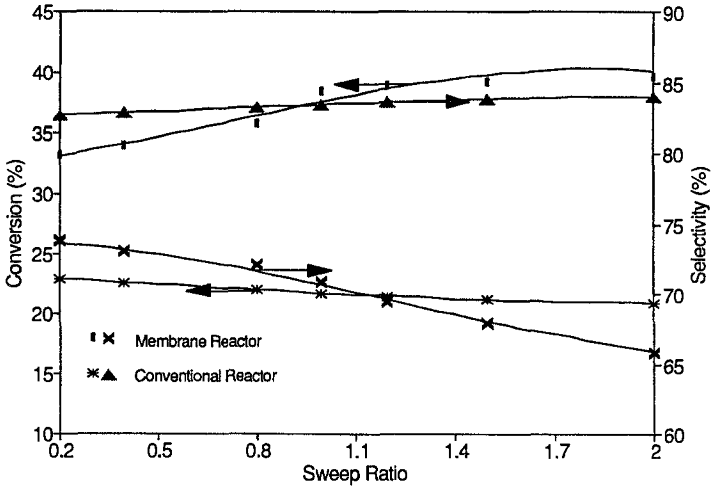

Fig. 9. Conversion and isobutylene selectivity versus sweep ratio for the reactant swept membrane reactor, $T = 500°C$, tubeside reactor residence time = 15 s.

been run, in which the membrane reactor was operated as a conventional reactor and the gas from the shellside inlet was directed to the tubeside of the membrane reactor. For example, for the membrane reactor experiment with a sweep ratio of 1 the corresponding conventional reactor experiment would have an isobutane inlet flow rate equal to the sum of the flow rates at the tubeside and shellside inlets of the membrane reactor, and an inlet molar composition of $i\text{-}C_4H_{10} : Ar : H_2$ of $1 : 0.1 : 0.1$. Note the significant gains in yields obtained in the membrane reactor in comparison with the yields in the conventional reactor. The selectivities for both reactors (see fig. 9) are smaller than those reported in the other figures, probably due to the higher isobutane to hydrogen ratio in the feed.

4. Conclusions

We have presented here the results of our experimental studies of the isobutane dehydrogenation reaction in a packed bed catalytic membrane reactor. Our experiments have shown that through the use of membrane reactors one can attain better conversions than those obtained in a conventional packed bed reactor operating under the same outlet pressure, and temperature and feed composition conditions. We believe that the conversions and yields reported here can be further improved by reactor and catalyst optimization. Work in this area is continuing.

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