

Dehydroisomerization Reaction in a Membrane Reactor: Thermodynamic Analysis

Giuseppe Barbieri^{*a}, Ilaria Mirabelli^b, Adele Brunetti^a, Enrico Drioli^{a,b}, Hamid A. Al-Megren^c, Mohamed Chafik Al-Kinany^c

^a Institute on Membrane Technology (ITM-CNR), National Research Council c/o The University of Calabria, Cubo 17C, Via Pietro Bucci, 87036 Rende CS, Italy

^b Chemical Engineering and Materials Department, The University of Calabria Cubo 45A, Via Pietro Bucci, 87036 Rende CS, Italy

^c King Abdulaziz City for Science & Technology, P.O. Box 6086, Riyadh 11442, Kingdom of Saudi Arabia
g.barbieri@itm.cnr.it

A study of a dehydroisomerization reaction in a membrane reactor has been carried out and the n-butane dehydroisomerization was chosen for its industrial relevance of the iso-butene, a useful product in MTBE and polymers production. The dehydroisomerization converts n-butane in isobutene with hydrogen production; therefore this reaction occurs with a mole number increase. The equilibrium conversion shift in a membrane reactor was evaluated taking into account the chemical equilibrium and the permeative equilibrium through a 100% hydrogen-selective membrane. In fact, the equilibrium in a membrane reactor also depends on the permeative equilibrium. This study focuses on the effect of the reaction pressure on the equilibrium conversion in a membrane reactor. In a traditional reactor, the equilibrium is thermodynamically not favored by the pressure increase owing to the increase of the moles number. In a membrane reactor, the reaction pressure driving the hydrogen permeation leads conversions four-five times higher than those achievable in a traditional reactor. When the hydrogen equilibrium partial pressure is set, the equilibrium conversion in a membrane reactor does not change changing the reaction pressure. This effect is related to the hydrogen stoichiometric coefficient and the moles number variation. For this reaction, the reactive equilibrium depends on both the reaction pressure and the hydrogen partial pressure with the same power of order equals one. When, moles number variation and hydrogen stoichiometric coefficient are equal each other, the hydrogen removal from reaction volume by permeation exactly balances the negative reaction pressure effect. Actually, the hydrogen equilibrium partial pressure sets the membrane reactor equilibrium conversion which depends only on it and not on the reaction pressure. A conversion of 0.83 and 0.33 are reached at 580°C when the hydrogen equilibrium partial pressure is equal 0.1 and 1 bar respectively.

Introduction

Among the butenes, isobutene is one of the important starting materials for the production of polymers and chemicals. The worldwide demand for isobutene and thus the production are expected to increase. In addition, dehydrogenation reactions of light alkanes have become more interesting research focus, due to their high H/C molar ratio and to the growing importance of the hydrogen.

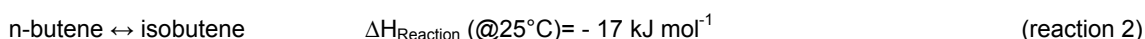
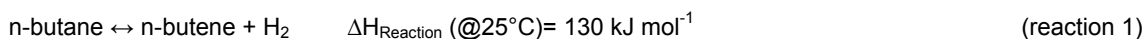
Currently, the C₄ fraction, 1-butene, cis-2-butene, trans-2-butene and isobutene, are usually obtained as by-products from petroleum refinery and petrochemical complexes that crack petroleum fractions and natural liquefied gas (Obenaus et al., 2005). Several technologies are emerging for the production of isobutene such as deep catalytic cracking and dehydrogenation of butanes. Butanes can be used as raw materials for the production of isobutene by isomerization and catalytic dehydrogenation to isobutene (Buonomo et al., 1997), resulting in a two-step process. This process is based on the propane dehydrogenation technology. Typically, in the dehydrogenation processes the conversion is equilibrium

limited and favored thermodynamically by low pressure and high temperature. An interesting alternative is the n-butane dehydroisomerization allowing the direct conversion of n-butane to isobutene via dehydrogenation and successive isomerisation (Scirè et al., 2004). The development and application of integrated processes, combining the reaction and separation in one single unit, pursuing the logic of Process Intensification (Stankiewicz and Moulijn, 2000) is increasingly becoming the focus of the chemical and industrial process. The membrane reactors (MRs), combining the reaction and separation in the same unit, seek this outcome very well. Moreover, the application of MRs is an interesting strategy, in particular for dehydrogenative-type reactions, equilibrium limited. In fact, the removal of hydrogen, by means of application of high H₂ selectivity membrane, can shift equilibrium, improving the conversion achievable. Isobutane dehydrogenation using catalytic MRs has been previously studied by many researchers. Some bi-functional catalytic systems, typically zeolite supported Pt catalysts, have been indicated as successfully catalysts for such direct conversion (Pirngruber et al., 1999).

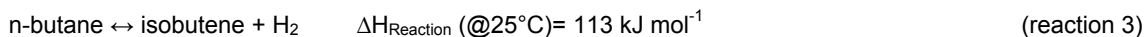
Different types of membranes, such as -alumina, zeolite MFI, Pd/Ag and Pd, dense silica and carbon molecular sieve membranes, have been investigated for this type of application. The general results show as in all cases a conversion above the equilibrium conversion of a traditional reactor (TR) could be obtained. In the present work, the shift in equilibrium conversion, resulting from the selective extraction of hydrogen in the MR, was evaluated by a thermodynamic analysis, taking into account chemical reaction equilibrium and permeative equilibrium through the membrane. The membrane reactor equilibrium was described using the model proposed by Barbieri et al. (2001). A simplified reactive scheme was used for a first analysis of the hydrogen removal on the reactive equilibrium considering a reduced chemical system. A Pd-Ag-based membrane, with infinite selectivity toward hydrogen, was taken into account. Since the equilibrium conversion is the maximum conversion achievable it can be useful defining how much an MR, with respect to a TR, can broaden the thermodynamic constraints for this reaction (Al-Megren et al., 2013). Equilibrium conversions achievable in a membrane and traditional reactors were discussed, investigating the effects of temperature, reaction pressure and equilibrium hydrogen pressure on the MR and TR.

Methods

The n-butane dehydrogenation is an endothermic reaction and occurs with an increment of mole numbers, thus the equilibrium conversion is favored by a high temperature and low pressure. To evaluate the reaction system composition at the equilibrium, the dehydrogenation and isomerisation can be considered as series reactions. The thermodynamic analysis was based on the following assumptions: no side-reactions occurring and only linear butene and isobutene production. The resulting simplified scheme, although more reactions and chemical species are actually involved, allows a comprehensive analysis of the conversion shift. For the dehydroisomerisation reaction the following simplified reactions model has been taken into account:



The reactions involved are the dehydrogenation of n-butane and successive isomerisation to isobutene (reactions 1 and 2). The dehydrogenation and isomerisation can be considered as a series reaction system and, if reactions 1 and 2 are "summed", the following reaction 3 is given.



The thermodynamic analysis for the membrane reactor is similar to the traditional reactor. In an MR the overall reaction unit can be considered as divided into two sectors: one part is the reaction volume and the other is the permeation volume. Through the hydrogen selective membrane, a part of hydrogen produced permeates through the membrane into the permeation side and the hydrogen removal from the reaction volume allows the reaction equilibrium shifting. As long as the hydrogen partial pressure in the reaction volume is greater than the partial pressure in the permeate side there is permeating flux. When the partial pressures of hydrogen, on both membrane sides, are equal no hydrogen permeation happens and then the permeative equilibrium is reached. The following equation was written by Marigliano et al. (2003) to describe the permeative equilibrium related to hydrogen permeation.

$$P_{\text{hydrogen}}^{\text{Equilibrium}} = P_{\text{hydrogen}}^{\text{Permeate side}} = P_{\text{hydrogen}}^{\text{Reaction side}} \quad (1)$$

Table 1 Moles number determination at reactive and permeative equilibrium in a membrane reactor

moles	n-butane	n-butene	isobutene	hydrogen
Initial state	n_0			
Reactive state of reaction 1	$-n_0x$	n_0x		n_0x
Reactive state of reaction 2		$-n_0xw$	n_0xw	
Permeation state				$-n_0xz$
Permeative and reactive equilibrium state	$n_0(1-x)$	$n_0x(1-w)$	n_0xw	$n_0x(1-z)$
Total moles number				$n_0(1+x-xz)$

$$K_{P1} = \frac{P_{\text{hydrogen}}^{\text{Reaction side}} P_{\text{n-butene}}^{\text{Reaction side}}}{P_{\text{n-butane}}^{\text{Reaction side}}} \quad (2)$$

$$K_{P2} = \frac{P_{\text{isobutene}}^{\text{Reaction side}}}{P_{\text{n-butene}}^{\text{Reaction side}}} \quad (3)$$

Therefore, the thermodynamic equilibrium in a membrane reactor depends on the permeative equilibrium, expressed by the above equation, in addition to the reactive equilibrium, expressed by equilibrium constants. Table 1 reports the reactive states for reaction 1 and 2 and also includes the information for hydrogen permeation through the variable “z”, which is the fraction of hydrogen in the permeation side compared to the total hydrogen produced. The difference with respect to TR is introduced by the negative term referred to the hydrogen permeation. Therefore, the moles number of each species at the equilibrium, reactive and permeative, is a function of the conversion degrees (x and w) of both reactions and hydrogen fraction permeated (z). The reactant and products distribution at reactive and permeative equilibrium can be evaluated from Table 1. The thermodynamic equilibrium in a membrane reactor depends on the permeative equilibrium expressed by the above equation 1 and reactive equilibrium. Equilibrium constant (Eq. 2 and 3) also take into account the permeation through the membrane by the z term. x, w and z are obtained solving Eqs. 1-3.

Results and discussion

The effects of temperature, reaction pressure and hydrogen equilibrium pressure have been investigated. Figure 1 shows the n-butane equilibrium conversion as a function of temperature reaction at different equilibrium hydrogen partial pressure. The trend is typical of an endothermic reaction: the conversion increases by increasing the temperature. Moreover, the effect of the equilibrium hydrogen partial pressure is also shown in Figure 1. When the partial pressure of hydrogen decreases, moving for instance from 1 to 0.1 bar, the equilibrium conversion of the membrane reactor strongly increases. In fact, for a temperature of 500°C, the equilibrium conversion achieved at lower hydrogen partial pressure, for a temperature of 500°C, is ca. three times that one at higher hydrogen partial pressure. The curves shown in figure 1 are the equilibrium conversion achievable in an MR at an equilibrium hydrogen partial pressure of 0.1 and 1 bar respectively, for any reaction pressure. The MR equilibrium conversion does not change varying the reaction pressure at a set equilibrium hydrogen pressure. In fact, in a traditional reactor the pressure negatively affects the reaction but the membrane reactor, through the removal of hydrogen from the reaction volume, overtakes this negative effect. A membrane reactor operating at 500°C gives an equilibrium conversion equal ca. 50%, for a hydrogen partial pressure at equilibrium of 0.1 bar. This value is three times higher than that can be obtained in a traditional reactor, operating at the same temperature and 5 bar as reaction pressure. In addition, a comparison between the n-butane equilibrium conversion (MREC) obtained in a membrane reactor and the equilibrium conversion in a traditional reactor (TREC), operating at the same reaction pressure, is shown in figure 2. Comparing the two curves, it can be noticed as, at high temperature, the membrane reactor shows a higher conversion with respect to the traditional reactor. At temperatures lower than 557°C, the TR equilibrium conversion obtained at 5 bar, exceeds the

membrane reactor equilibrium conversion (MREC) because of the hydrogen back-permeation. In fact, at low temperature, the conversion is low and consequentially the partial pressure of hydrogen present in the permeate side leads to a back-permeation. Moreover, since the partial pressure of hydrogen is kept constant, the equilibrium conversion of the membrane reactor is the same at any reaction pressure. The evaluation of the distance between the MREC and TREC, operating at the same conditions, appears of interest to estimate in which condition the MR compared to the traditional shows the highest reachable conversions. To quantify this distance the conversion index, already defined by Brunetti et al. (2007), was used. This variable, calculated at the equilibrium condition, is the ratio of equilibrium conversion in an MR and TR. Figure 3 shows the ratio of membrane reactor and traditional reactor equilibrium conversion as a function of temperature at the reaction pressure of 10 bar and equilibrium hydrogen partial pressure of 0.1 bar. The MREC exceeds the TREC in the whole temperature range investigated and the curve shows a maximum as a function of temperature. The presence of a maximum is due to the thermodynamic effect on the reaction at both low and high temperature. In fact, at high temperature, the reaction is thermodynamically favored and MREC and TREC tend to unitary value. Therefore, the contribution of the equilibrium shift on the equilibrium conversion is not significant. At low temperature the MREC is similar to the TREC, because of the thermodynamics and consequentially of the back permeation. In the intermediate range of temperature the MR shows the best performance. A MREC value 5 times higher than TREC is achieved at 500°C.

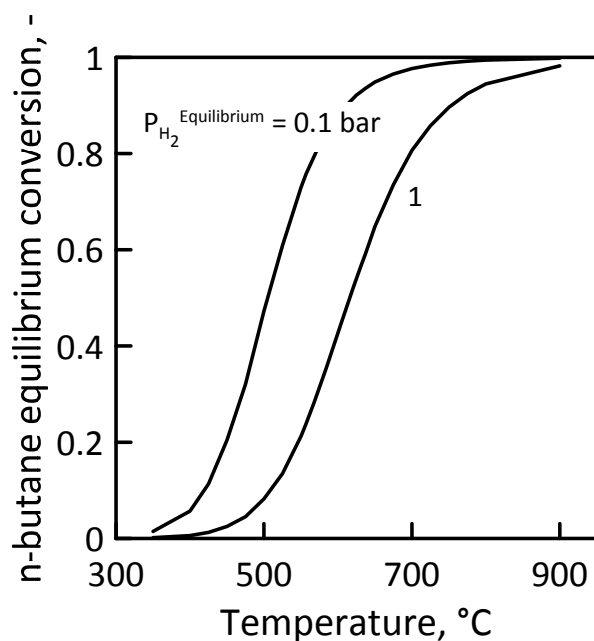


Figure 1: *n*-Butane dehydroisomerisation (reaction 3): membrane reactor equilibrium conversion (MREC) as a function of temperature at different equilibrium hydrogen partial pressure.

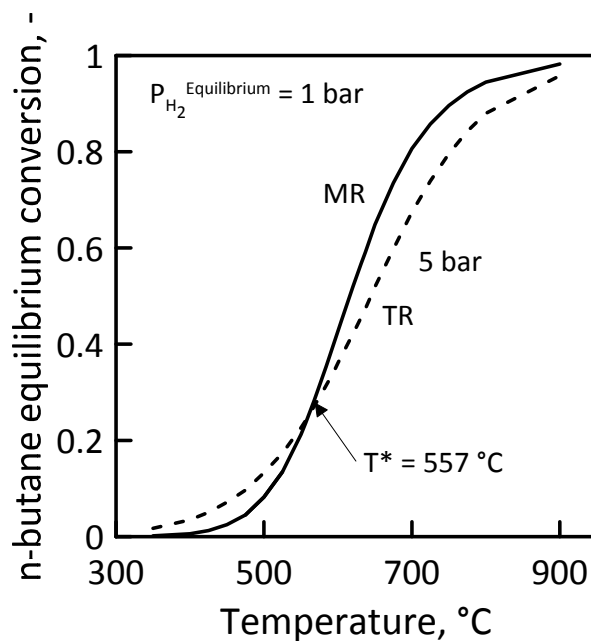


Figure 2: *n*-butane dehydroisomerisation (reaction 3): membrane reactor equilibrium conversion and traditional reactor equilibrium conversion as a function of temperature. Reaction pressure 5 bar, permeate pressure = 1 bar

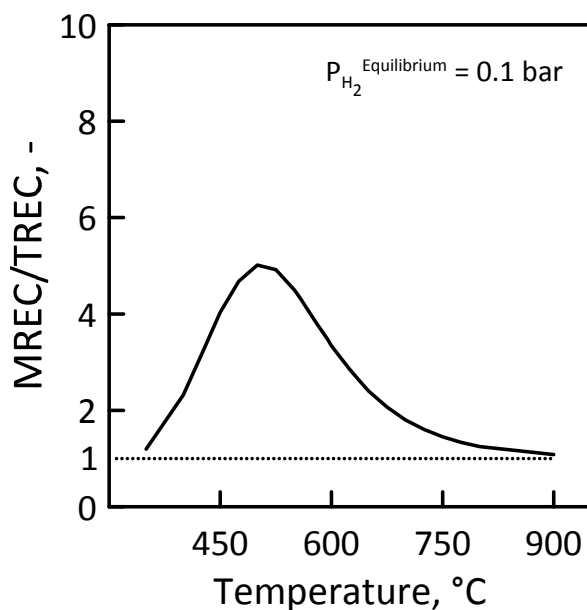


Figure 3: Comparison of membrane reactor equilibrium conversion (MREC) and traditional reactor equilibrium conversion (TREC) as a function of temperature. Reaction pressure 10 bar and equilibrium hydrogen partial pressure 0.1 bar.

Conclusions

The shift in equilibrium conversion, as a result of selective extraction of hydrogen carrying out the *n*-butane dehydroisomerization in a membrane reactor was evaluated. The chemical reaction and permeative equilibria were taken into account to describe the equilibrium in the membrane reactor. On the basis of analysis performed, the membrane reactor equilibrium conversion depends on the hydrogen equilibrium partial pressure and does not change varying the reaction pressure. In fact, increasing the hydrogen partial pressure increases the amount of hydrogen removed from the reaction volume which promotes the

equilibrium shift. In addition, since the reaction has an increase in the mole numbers, the reaction pressure affects the equilibrium conversion. While in a traditional reactor, the reaction pressure increasing has a negative effect and leads to a lower equilibrium conversion, in a MR this effect is balanced by the equilibrium shift due to the hydrogen permeation. The analysis performed also provides an estimation of optimum conditions, in the temperature and pressure range investigated, which allow achieving the highest reachable conversions in a membrane reactor compared to that of the traditional one. A membrane reactor operating at 500°C, 10 and 0.1 bar as reaction and equilibrium hydrogen partial pressures, respectively, achieves a conversion five times higher than that obtainable in a TR. This value gives a powerful indication of how the membrane reactor application can broaden the thermodynamic constraints for dehydrogenative-type reactions.

References

- Al-Megren H.A., Barbieri G., Mirabelli I., Brunetti A., Drioli E., Al-Kinany M.C., "Direct conversion of n-butane to isobutene in a membrane reactor: a thermodynamic analysis", *Ind. & Eng. Chem. Res.*, 2013, <http://dx.doi.org/10.1021/ie400006c> *accepted*
- Barbieri G., Marigliano G., Perri G., Drioli E., 2001, Conversion-Temperature Diagram for a Palladium Membrane Reactor. Analysis of an Endothermic Reaction: Methane Steam Reforming, *Ind. Eng. Chem. Res.* 40, 2017.
- Brunetti A., Caravella C., Barbieri G., Drioli E., 2007, Simulation study of water gas shift reaction in a membrane reactor, *J. Mem. Sci.* 306(1-2), 329-340.
- Buonomo F., Sanfilippo D., Trifirò F., Ertl G., Knozinger H., Weitkamp J., Eds., 1997, Handbook of Heterogeneous Catalysis, vol 5: Dehydrogenation reactions, Wiley-VCH, Weinheim, Germany.
- Marigliano G., Barbieri G., Drioli E., 2003, Equilibrium conversion for a Pd-based membrane reactor. Dependence on the temperature and pressure, *Chem. Eng. and Processing* 42, 231-236.
- Obenaus F., Droste W., Neumeister J., Wiley-VCH Eds., 2005, Ullmann's Encyclopedia of Industrial Chemistry, Butenes.
- Pirngruber G. D., Seshan K., Lercher J. A., 1999, Dehydroisomerization of n-Butane over Pt-ZSM5 (I): Effect of the Metal Loading and Acid Site Concentration, *Journal of Catalysis* 186, 188-200.
- Scirè S., Burgio G., Crisafulli C., Minicò S., 2004, Dehydroisomerization of n-butane over H-Y zeolite supported Pt and Pt,Sn catalysts, *Applied Catalysis A: General* 274, 151-157.
- Stankiewicz A., Moulijn J. A., 2000, Process intensification: Transforming chemical engineering, *Chem. Eng. Prog.* 96(1), 22-23.