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# An analysis of the Peclet and Damkohler numbers for dehydrogenation reactions using molecular sieve silica (MSS) membrane reactors

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## Abstract

The use of membrane reactors in industrial processes leads to high efficiencies because the reaction equilibrium can be shifted towards high conversion and product formation. In addition, the combination of reaction and separation in a single unit operation leads to process simplification and probably hardware cost reduction. A key design factor for membrane reactors is the ratio of maximum reaction rate per volume over maximum permeation rate per volume, characterised by the product of Damkohler and Peclet numbers (*DaPe*). The smaller the *DaPe* number, the more effective the membrane reactor becomes. Using a membrane bed reactor with molecular sieve silica (MSS) membranes and the dehydrogenation of cyclohexane to benzene as the test reaction, we observe that cyclohexane conversion rates increased from 3% to 20% as the *DaPe* reduced from 80 to 1. The conversion is well predicted by a simple equilibrium model. The *DaPe* number provides a simple measure of the interaction of the reaction and separation effects and a method to evaluate the membrane reactor efficiency to optimise the design.

*Keywords:* Damkohler and Peclet numbers; Molecular sieve silica; Membrane reactors; Modelling; Cyclohexane; Dehydrogenation

## 1. Introduction

The two most important, and often the most expensive steps in a chemical process are the chemical reaction operations and the subsequent separation of the product streams [1]. Membrane reactors, which provide a method for simultaneous reaction and product separation, can offer many benefits over more conventional systems which apply these operations in series. This is especially the case where in situ product separation can enhance an equilibrium limited reaction [2,3]. Saracco et al. [4] noted the major potential of membrane reactors for equilibrium enhancement in dehydrogenation reactions, because they are endothermic and equilibrium limited. These reactions are favoured at high temperatures, but under these conditions side reactions become significant, reducing reactor selectivity and deactivating the catalyst [5,6]. Membrane reactors provide an opportunity to obtain high conversions at lower temperatures, thus reducing undesirable reactions and improving the product yield [7].

In a conventional packed bed reactor two important rates govern its performance—the rate of reaction and the rate of convective transport of the reactant feed [1]. The ratio of these is the Damkohler number (*Da*), an important dimensionless number characterising conventional transport reactors. For membrane transport, the relative importance of the convective transport versus permeation, given also by the ratio, is the Peclet number (*Pe*). The product of the Damkohler and Peclet numbers (*DaPe* number) provides the ratio of maximum reaction rate per volume over maximum permeation rate per volume, a defining feature of a membrane reactor. As the reaction rate is related to the proportional concentration of products to reactants, then *DaPe* number provides a convenient parameter to analyse the efficiency of the reaction and thus the activity of the catalyst. The relationships between reactor conversion, selectivity and *Da* and *Pe* have been explored by Moon and Park [8].

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**Nomenclature**

| | |
|---|---|
| $A_m$ | membrane surface area ($m^2$) |
| $C_i$ | concentration of component $i$ ($mol\ m^{-3}$) |
| $Da$ | Damköhler number |
| $DaPe$ | Damköhler–Peclet number |
| $E_a$ | reaction activation energy ($kJ\ mol^{-1}$) |
| $F_c^0$ | initial cyclohexane flow rate ($mol\ s^{-1}$) |
| $k_r$ | reaction rate constant ($mol\ m^{-3}\ Pa^{-1}\ s^{-1}$) |
| $K_B$ | adsorption equilibrium constant of benzene ($Pa^{-1}$) |
| $K_p$ | reaction equilibrium constant ($Pa^3$) |
| $Pe$ | Peclet number |
| $P_r$ | reactor pressure (Pa) |
| $Q_i$ | permeance ($mol\ m^{-2}\ Pa^{-1}\ s^{-1}$) |
| $r_c$ | reaction rate expression ($mol\ m^{-3}\ s^{-1}$) |
| $V_r$ | catalyst volume ($m^3$) |
| $X_i$ | conversion |

*Greek symbol*

| | |
|---|---|
| $\rho_i$ | partial pressure of component $i$ (Pa) |

In recent years, several studies have been done on the cyclohexane dehydrogenation reaction in membrane reactors [6,9–11]. Itoh and Wu [2] first studied this reaction experimentally and theoretically over porous Vycor glass and palladium membranes, developing a plug flow and isothermal model for the reaction. This model looked at the effects of feed rate and sweep gas on the conversion and achieved good agreement between the model and experimental data. Kokugan et al. [11] also investigated this reaction using three different types of membranes in a cylindrical tube reactor with a large volume of catalyst packed in the tube side. An equilibrium model was then used to look at the effect of changing Damkohler number on conversion, with increasing pressure across the membrane.

While these studies have investigated the effects of operating conditions on reactor conversion, very little study has been taken into the effect of membrane permeance on conversion for optimisation of catalyst weight. While the permeance in palladium membranes is related mainly to the palladium thickness, in silica membranes there are considerably more variables that can affect this, including pore size, pore size distribution, membrane thickness and temperature [12–15]. With the recent improvements in the structural properties of silica membranes leading to increased permeation and selectivity, there is a need to investigate the effects of these improvements on membrane reactor processes.

This work explores the operation of a low temperature packed bed membrane reactor (PBMR) for the dehydrogenation of cyclohexane to benzene using MSS membranes and platinum catalysts. This reaction is well characterised in the literature and provides a convenient basis for the focus of this work, namely the use of the *DaPe* number applied to conversion and permeation in a PBMR. The relevant reaction is:

$$C_6H_{12} \leftrightarrow C_6H_6 + 3H_2 \quad \Delta H^0 = 205.7\ kJ\ mol^{-1} \qquad (1)$$

This reaction is equilibrium controlled and if benzene and hydrogen are preferred products, the equilibrium can be forced to the right by removal of hydrogen from the reaction mixture. We use membranes with different permeation rates to investigate the effect of hydrogen separation on the conversion of cyclohexane to benzene.

## 2. Experimental

Four MSS membranes of varying quality were synthesized for use in this study. These membranes were produced using an acid catalysed two-step sol–gel process dip coated on a porous ceramic support, as reported elsewhere [16,17]. As shown in Fig. 1, the membranes had a porous substrate made of α-alumina, a less porous thin layer of γ-alumina which was used to deposit a thin MSS film of 250 nm thickness. The membranes were initially tested using a dynamic permeation apparatus to check the membrane quality for $H_2$ permeation and corresponding activation energy for temperatures ranging from 150 to 250 °C. The system was limited to a maximum operating temperature of 250 °C due to the o'ring seals in the reactor.

A plate-type, packed bed membrane reactor was used for this study as depicted in Fig. 2. The membrane reactor had an effective permeation area of 1.25 $cm^2$ and reactive length of 18 cm with the membrane placed in direct contact with the pelletised catalyst. The experiments used a commercial Pt/$Al_2O_3$ catalyst containing 0.5 wt.% Pt supported on porous

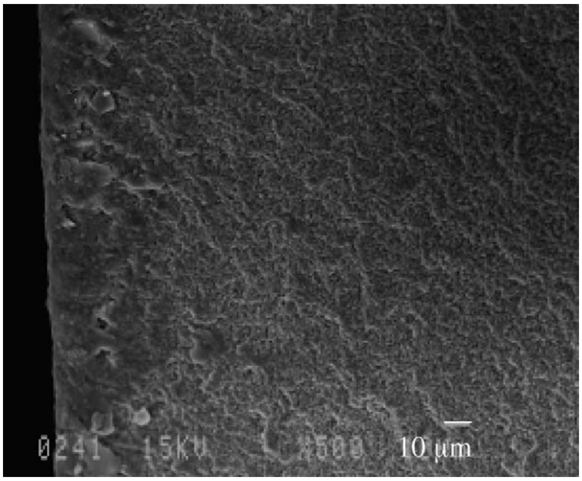

Fig. 1. Scanning electron micrograph of a MSS membrane profile.

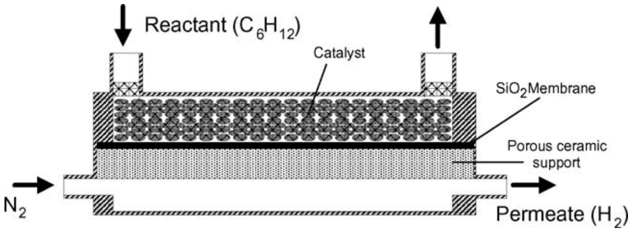

Fig. 2. Cross-section of the packed bed membrane reactor.

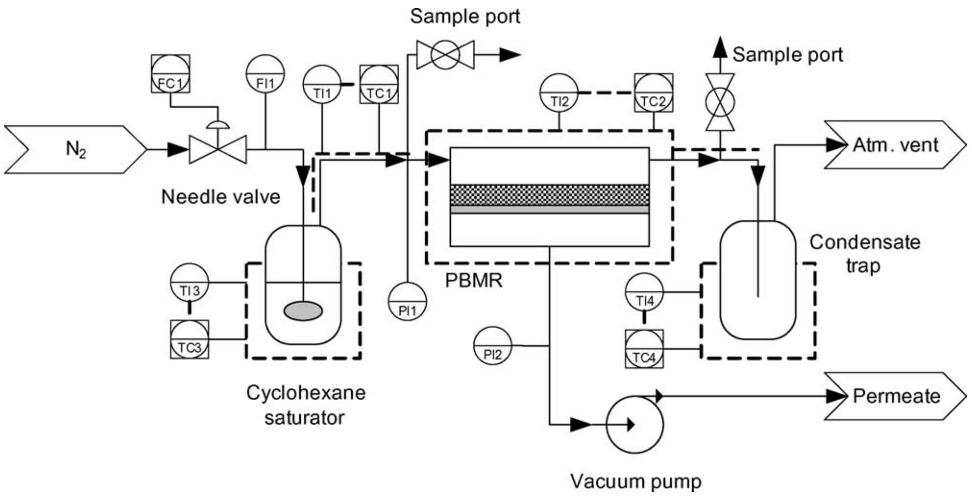

Fig. 3. Experimental PBMR setup.

γ-alumina (particle size = 149–210 μm, BET surface area = 184.3 $m^2 g^{-1}$). The $Pt/Al_2O_3$ catalyst was prepared by an impregnation method at ambient temperature over a 24 h period in an aqueous solution of hydrogen hexachloroplatinate ($H_2PtCl_6$). The catalyst was then dried in air at 110 °C for 24 h, and was then calcined in air at 400 °C for 3 h. The reduction of the catalyst was subsequently carried out under flowing hydrogen for 10 h at 400 °C. 0.3 g of catalyst was used in the membrane reactor tests while 2–3 g was used in conventional reactor tests with glass wool used to provide an even distribution of catalyst along the reactor length.

All tests were carried out in an experimental membrane reactor setup as shown in Fig. 3. A $N_2$ flow of 100 ml $min^{-1}$ was passed through the cyclohexane saturator at ~72 °C providing a cyclohexane feed of $3.15 \times 10^{-3}$ mol $s^{-1}$, equivalent to a cyclohexane molar concentration of 47% at the feed stream. A pipe with heating tape was used to transmit the cyclohexane vapour to the membrane reactor, which was operated at a temperature and pressure of 250 °C and 1 atm. The retentate from the membrane reactor was subsequently condensed and then analysed using a Shimadzu GC 17A with TCD detector. Tests were also carried out in a conventional packed bed reactor using the same catalyst and experimental conditions in order to provide a performance comparison.

SEM samples were prepared by fracturing a membrane cross-section then coated with platinum. SEM of the fracture surface was performed using a JEOL JSM-890 SEM at an accelerating voltage of 20 kV.

## 3. Results and discussion

The simulation of a packed bed membrane reactor was based on the assumptions of (i) plug flow within the reactor section, (ii) isothermal conditions, (iii) ideal gas behaviour, and (iv) the membrane is permeable to $H_2$ only. In equilibrium controlled reaction, changes in the component concentrations can be defined using Le Chatelier's principle based on the relative partial pressures of each component, which rearranged in terms of molar concentration gives:

$$K_p = \frac{[C_H]^3[C_B]}{[C_C]}\left(\frac{P_r}{C_T}\right)^3 \qquad (2)$$

Where:

$$C_T = C_C + C_H + C_B + C_I \qquad (3)$$

If only cyclohexane and inert nitrogen are fed into the reactor bed and only pure hydrogen can significantly permeate through the separation membrane layer then the product concentration can be modeled using equilibrium calculations [11]. While product concentrations are calculated from partial pressures, the equilibrium constant ($K_p$) is a thermodynamic property of the system and is calculated from the Gibbs's free energy of formation equation. This sets the variable concentrations at the outlet for the membrane reactor. Knowing the equilibrium constant, Eq. (2) can now be solved numerically to give the theoretical equilibrium conversion of the reaction. The results of these conversions are shown in Fig. 4, which considers the effect of $H_2$ separation on the conversion of cyclohexane with

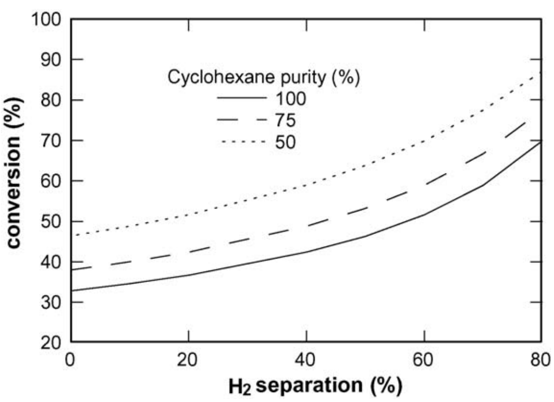

Fig. 4. Effects of $H_2$ separation on cyclohexane conversion at varying feed concentrations. Feed dilution is by nitrogen at 250 °C, 1 atm pressure.

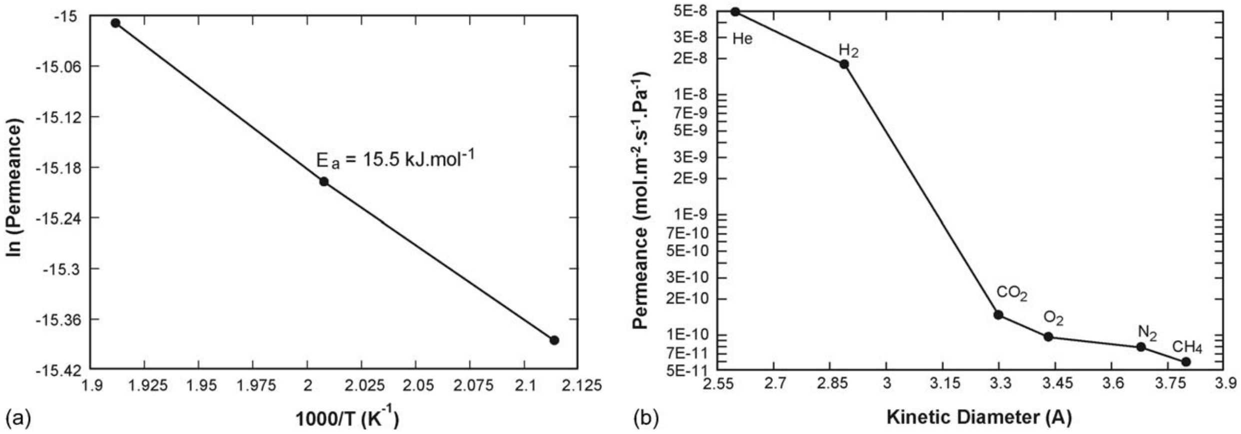

Fig. 5. (a) Arrhenius plot for the permeation of membrane M1 at $\Delta P = 1$ atm. (b) Permeation of membrane M3 at 150 °C and $\Delta P = 1$ atm.

varying concentration of inert gas. However, this calculation gives no indication of the mass of catalyst needed to achieve this conversion. The Damkohler number (Eq. (6)) can be used to analyse the effect of catalyst weight.

Fig. 5(a) depicts the $H_2$ permeation of the MSS membranes used for the experiments. The permeation increased as a function of temperature, indicating activated transport. The apparent activation energy ($E_a$) of $15.5\ \mathrm{kJ\,mol^{-1}}$ for $H_2$ permeation was determined using a classical Arrhenius relationship. This value was in excess of $10\ \mathrm{kJ\,mol^{-1}}$, indicating that high quality membranes were produced [18,19]. Both activated transport and high $E_a$ results showed that molecular sieving was the prevalent transport mechanism.

Fig. 5(b) shows a relative pore size distribution using the permeance as a function of molecular probes. High selectivities (i.e. gas permeance ratios) were achieved. For instance, the permeation of the small kinetic diameter molecules (He and $H_2$) was up to three orders of magnitude higher than the larger molecules ($O_2$, $N_2$ and $CH_4$). As the kinetic diameter of cyclohexane ($d_k = 6.1$ Å) and benzene ($d_k = 5.1$ Å) are much larger than $CH_4$ ($d_k = 3.8$ Å), permeation of cyclohexane and benzene may be expected to be several orders magnitude lower than $H_2$ ($d_k = 2.9$ Å). These membranes clearly show the ability of allowing the small molecules ($H_2$) to diffuse through while hindering the passage of the larger molecules (cyclohexane and benzene).

The ability of the membrane to process one of the products in the reaction can be determined from the permeation experiments. The hydrogen Peclet number (Pe), Eq. (4), provides a measure of the gas flux out of the reactor by permeation (taken to be all $H_2$) against the transport flux through the reactor (the theoretical amount of $H_2$ produced by reaction assuming complete conversion and no removal)

$$\frac{1}{Pe} = \frac{Q_i A_m P_r}{3F_c^0} \tag{4}$$

In the experiments reported here, the inlet flux, membrane areas and reactor pressure are all constant, but the different membranes provide different *Pe* numbers, since they have different permeation properties. The dehydrogenation reaction rate of cyclohexane over $Pt/Al_2O_3$ can be expressed as follows [2]:

$$r_C = -\frac{k_r(K_P \rho_C/\rho_H^3 - \rho_B)}{1 + K_B K_P \rho_C/\rho_H^3} \tag{5}$$

In a membrane reactor, it is possible to maximise the reaction rate by removing $H_2$ as quickly as it is formed. From Eq. (5), the reaction rate for a given gas mixture is set mainly by the rate constant $k_r$, which depends on the mass of catalyst, according to the relationship [11]

$$Da = \frac{k_r P_r V_r}{F_c^0} \tag{6}$$

The Damkohler number relates the rate of reactant feed per catalyst volume to the reactor, given an indication of the rate of reaction over the convective transport flux. A sufficiently high *Da* number is necessary to drive the reaction to equilibrium, for this reaction typically about 5 [11]. If the *Da* number is lower, then the residence time in the reactor is insufficient for equilibrium to be reached and there is a relative approach to equilibrium. In the experiments here, all of the parameters in Eq. (6) remained the same, and therefore the *Da* number was also constant. For the conditions chosen (inlet flow, catalyst load, temperature, pressure), the approach to (pseudo-) equilibrium in the reactor was found to improve with increasing permeation. Pseudo-equilibrium refers to the condition where one (or more) of the reaction products is independently manipulated, in this case by the use of the $H_2$ permeable membrane.

An important tool for characterising a membrane reactor is the product of the Damkohler and Peclet numbers, *DaPe*, which relates the rate of product by reaction with the rate of its removal by permeation

$$DaPe = \frac{k_r P_r V_r}{Q_i A_m P_r} \tag{7}$$

This relationship dictates the effectiveness of a membrane reactor. If *DaPe* equals to 1, then all of the $H_2$ that is generated by reaction is removed through the membrane. There is no advantage to having a $DaPe < 1$, with the implication that the reactor throughput could be increased, since the reactor capacity is not being fully utilised. In other words the $DaPe = 1$ is

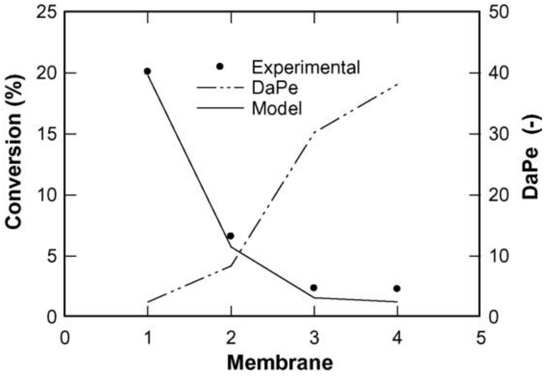

Fig. 6. Effect of membrane type and reactor temperature on conversion at 250 °C.

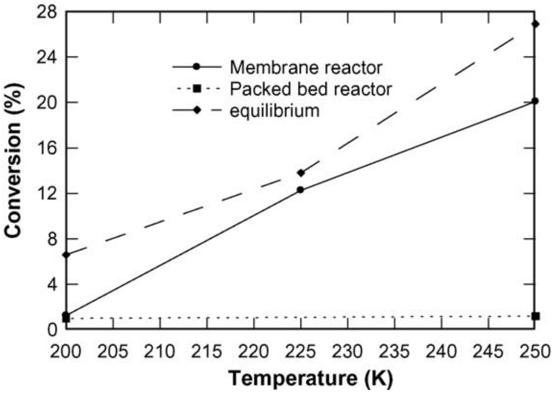

Fig. 7. Membrane reactor results compared to thermodynamic equilibrium.

the limit and equivalent to the maximum permeation possible to match the reaction rate. For a set production rate, Eq. (7) consequently gives the quantity of catalyst that is required. If $DaPe > 1$, then $H_2$ builds up in the reactor and productivity is constrained by an inadequate membrane.

As *DaPe* analyses the relative amount of $H_2$ left in the reactor, it can be used to predict the relative reaction rate and hence conversion when pseudo equilibrium is not being reached. In this case actual conversion was calculated by the following equation for $DaPe > 1$:

$$X_{\text{actual}} = \frac{X_{\text{equilib}}}{DaPe} \tag{8}$$

In Fig. 6, the model above discussed shows the *DaPe* trend against cyclohexane conversion for four membranes with varying permeation rates. The model gave a good fitting to the experimental results with the *DaPe* number accurately predicting the reactions approach to equilibrium. Membrane M1 $H_2$ permanence was $2 \times 10^{-7}\ \text{mol m}^{-2}\,\text{s}^{-2}\,\text{Pa}^{-1}$ whilst membranes M3 and M4 resulted in one order magnitude lower values. At the same time, cyclohexane conversion was low (<3%) for the membrane reactors using low permeation membranes M3 and M4, but increased to 20% using high permeation membrane M1. This gives a strong indication that membranes M3 and M4 could not process or separate $H_2$ fast enough from the reaction chamber, thus limiting the reaction and resulting in similar conversions as a conventional packed bed reactors (see Fig. 7) under similar experimental conditions.

Using the Gibbs equation the equilibrium conversion was plotted in comparison with the experimental results (Fig. 7). It is observed that conversion increased with temperature as the activity of the catalyst and equilibrium point increased accordingly. These conversions were still generally low, being limited by experimental temperatures of up to 250 °C due to o'ring maximum operating temperature. While the limited size of the reactor was unable to provide the desired high conversion, through optimisation of the *DaPe* number this can be offset by increasing the catalyst efficiency.

It is known that large volumes of catalyst provide the driving force to exceed equilibrium. In the operation of a membrane reactor where $H_2$ is selectively removed during reaction, it is expected that higher conversions will be obtained. However, the current results under low catalyst volumes showed that the membrane permeance reached a balance with the catalyst reaction hence producing a faster reaction. This relationship as shown by the *DaPe* number (Eq. (7)) gives an indication of the systems ability to operate at its most efficient point. On the other hand, the packed bed reactor resulted in very low conversion of less than 3% over the temperature range tested. As the $H_2$ concentration increased over the packed bed reactor length, the reaction slowed considerably limiting the overall conversion.

Fig. 8 shows the increase in conversion found by decreasing the *DaPe* for a set amount of catalyst. Through use of high quality membranes the production rate per mass of catalyst was increased 80 times over that produced in the conventional bed reactor. This allowed the membrane reactor to provide significantly higher conversion even though 1/10th the catalyst was used. It is also observed that there is a definable point where small changes in *DaPe* start having a large effect on the conversion. For these experiments this point corresponded to a *DaPe* of less than 10. However, as the reaction increases exponentially the permeation must be considerably higher to provide any additional benefit, otherwise the reaction rate provides the limit of this system model. As the permeation increases the *DaPe* will theoretically reach a minimum of 1.

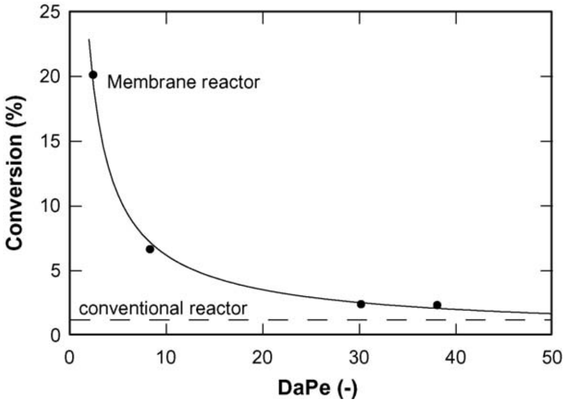

Fig. 8. Conversion vs. *DaPe* at 250 °C using different permeation rates.

This corresponds to the point where all hydrogen is being removed as it is produced. Therefore, the reaction is always at its maximum thus behaving like a first order reaction. Conversely as the *DaPe* increases above 40 it is seen that the conversion levels out and the reactor starts behaving more like a conventional packed bed reactor. In this case any change in permeance has little effect on the reaction rate as the reaction becomes saturated with hydrogen quickly.

## 4. Conclusions

MSS membranes were used in a packed bed membrane reactor assembly to investigate cyclohexane conversion to benzene at a temperature range from 200 to 250 °C. High $H_2$ apparent activation energy of 15.5 kJ $mol^{-1}$ was achieved whilst $H_2$ selectivities in excess of 1000 were calculated to benzene and cyclohexane, indicating that the membranes used were of high quality and defect free. High $H_2$ permeation membranes allowed for the catalyst to operate at its optimum state of high conversions at 20% at 250 °C, leading to a *DaPe* theoretical minimum of 1. With low permeation membranes, the *DaPe* increased to values up to 40, whilst conversions decreased to less than 3%. Higher *DaPe* are directly related to low permeation rates. In this case, the membrane is unable to process or separate $H_2$ fast enough from the reactor chamber and behaves like a conventional packed bed reactor, as the product reaction rate is much higher than the permeation rate. The analysis of the packed bed membrane reactor optimisation was provided through the use of the *DaPe* number, and calculating the relative reaction to permeation of hydrogen within the reactor. It was found that as the permeation rate became equal to the reaction rate the catalyst worked at its optimum rate and so the best conversions below pseudo-equilibrium could be achieved.

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