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## CATALYTIC COMBUSTION OF PROPANE IN A MEMBRANE REACTOR WITH SEPARATE FEED OF REACTANTS—II. OPERATION IN PRESENCE OF TRANS-MEMBRANE PRESSURE GRADIENTS

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**Abstract**—This is the second communication of a series dealing with an experimental and modelling study on propane catalytic combustion in a membrane reactor with separate feed of reactants. In paper I the behaviour of the reactor in the absence of trans-membrane pressure gradients was presented and discussed. Attention is here focused on the reactor behaviour when pressure differences are applied over the membrane, resulting in a convective flow through the membrane itself. By these means, a major conversion enhancement (up to more than 300%) is achievable compared to the case in which only diffusive mass transfer controls the reactor performance. However, above certain pressure differences ( $> 1$  bar), this is obtained at the price of noticeable slip of unconverted reactants across the membrane. The experimental results are in good agreement with the predictions of an isothermal model based on the numerical solution of differential mass balances across the membrane, employing a Stefan–Maxwell expression for diffusive fluxes and a d’Arcy law for convective ones.

### 1. INTRODUCTION

The most peculiar features of catalytic membrane reactors with separate feed of reactants for application to hydrocarbon combustion were enlightened in paper I (Saracco *et al.*, 1995): avoidance of any pre-mixing of reactants with no formation of explosive mixtures, low sensitivity to thermal runaways, good flexibility and easy controllability, possibility to improve the reaction selectivity towards partial oxidation products, etc. The basic scheme of this reactor type is outlined in Fig. 1.

The above communication was the first of a series concerning a pilot plant study on propane catalytic combustion in a Pt/ $\gamma$ - $\text{Al}_2\text{O}_3$ -activated membrane. Attention was there paid on operation of the reactor in the absence of any pressure difference over the membrane and modelling thereof.

In this second communication the effect of the application of a pressure gradient across the membrane is studied. Earlier studies based on CO oxidation (Veldsink, 1993), used as a model reaction, demonstrated how this is an effective means to increase the

overall conversion achievable, without losing, within certain limits, most of the interesting properties enabled by this reactor concept.

Further, an isothermal model suitable for predicting the performance of the reactor in such operating conditions is presented. Such a model is based on a system of differential mass balance equations for the various components of interest, accounting for both convective and diffusive mass transfer contributions, and solved for two different sets of boundary conditions (either considering or neglecting the mass transfer resistance in the gas phases outside the membrane). The much higher complexity of this model, which needs a numerical solution method, compared with that of the model presented in the previous paper of this series, which could be analytically solved, entails the need of further characterisation studies on the prepared membrane reactor, concerning either the membrane permeability or the assessment of reaction kinetics in the membrane itself.

### 2. THEORY

Earlier studies about transport of multicomponent mixtures in porous slabs, facing different gas mixtures

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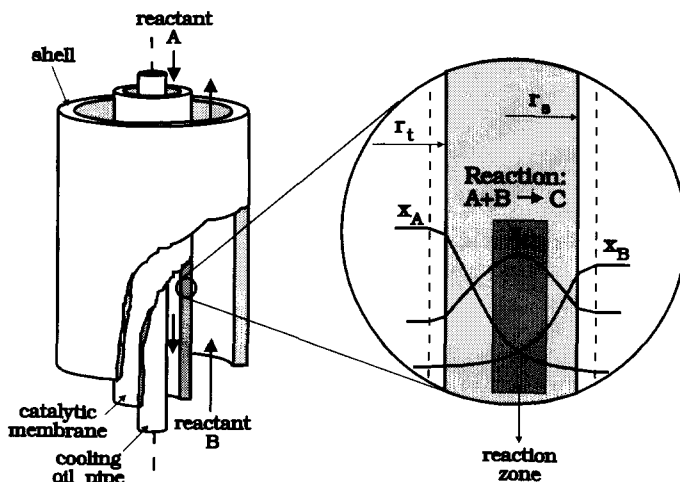


Fig. 1. Scheme of the tubular membrane reactor setup.

at opposite sides, demonstrated that a Stefan–Maxwell approach for the prediction of mole fluxes is to be preferred to the Fickian one especially when pressure differences over the membrane are applied (Veldsink *et al.*, 1992). The dusty-gas-model (Mason and Malinauskas, 1983), based on irreversible-thermodynamics concepts, proved to be a reliable tool. Mole fluxes of each component have to be combined with reaction and accumulation terms in the formulation of differential mass balances.

Table 1 summarises the required model equations in case of a tubular membrane under isothermal conditions. Different sets of possible boundary conditions at the membrane interfaces are outlined as well.

The hydrodynamics characterisation of the reactor chambers, presented and discussed in paper I (Saracco *et al.*, 1995), lead to the conclusion that a plug-flow behaviour can be assumed with confidence for both chambers for the feed flow rates employed in this study. Hence, the partial pressures at the membrane interfaces (in case the external mass transfer is neglected) or in the bulk of the reactant feeds (when the external mass transfer is accounted for) were assumed to be equal to the logarithmic mean between the values of the partial pressures at the inlet and the outlet of each chamber.

The model was solved through a Pascal computer code based on the finite difference method, and was implemented on a VAX (VMS) station. Details about the numerical solution technique are given by Veldsink (1993) for Dirichlet-type boundary conditions (see Table 1). Instationary mass balances had to be used because of stiffness problems which arise when operating with fast kinetics and high pressure differences over the membrane. The stationary solution was assumed to be the limit to the series of dynamic solutions derived at progressive time steps. This model setup will be named 'model D'.

For the second type of boundary conditions (i.e. equality of internal and external mole fluxes for each

component at membrane interfaces) the direct inclusion of the boundary equations in the overall system of finite-difference equations turned to give high instability to the numerical solution. Convergence was difficult to attain unless very low external mass transfer resistances were considered. Therefore the solution of the model equations was attained via a two-step procedure: an inner routine solved the system of mass balances using fixed boundary concentrations, while an outer routine adjusted the interfacial concentrations of each component in order to fit the boundary equations iteratively. Overall convergence was thus attained slower for this model setup (named hereafter 'model E') than for model D, but the former model is a better approximation of reality. Later on the applicability of both models will be discussed.

In any case, the effective diffusion coefficients were calculated via the Bosanquet expression, accounting for both Knudsen and bulk contributions

$$D_i^e = 1/(1/(4/3)K_0\sqrt{8RT/\pi M_i} + 1/(\varepsilon/\tau)D_i^g) \quad (1)$$

in which the Fuller–Schettler–Giddings equation was chosen for  $D_i^g$  (Reid *et al.*, 1987).

Further, note that if high pressure differences are imposed over the membrane, resulting in a one-way convective flow which overrules diffusive rates, the partial pressure gradients in the external boundary layers are not anymore simply inversely proportional to  $k_{gi}$ , but become a complex function of the fluxes of each component at the membrane interface, as suggested by Bird *et al.* (1960). In any case  $k_{gi}$  remains by definition the external mass transfer coefficient in the absence of any convective flow through the membrane. This parameter can be evaluated, as already mentioned in paper I (Saracco *et al.*, 1995), on the basis of the Chilton–Colburn analogy and the work of Lundberg *et al.* (1963), regarding the solution of the problem of heat transfer in laminar regime across annular passages between walls having different temperatures (see the scheme of the reactor setup shown

Table 1. Isothermal model for a tubular membrane reactor with separate feed of reactants

Mass balances of each component: $\frac{\varepsilon}{RT} \frac{\delta p_i}{\delta t} = -\frac{1}{r} \frac{\delta(rN_i)}{\delta r} + \mathcal{R}_i$
Mole fraction consistency: $\sum p_i = \sum x_i P = P$
Reaction terms: $\mathcal{R}_i = f(T, p_i, \dots)$ , $\mathcal{R}_{\text{inert}} = 0$
Flux terms (Dusty-gas-model):
$\sum_{j=1, j \neq i}^n \frac{x_i N_j - x_j N_i}{D_{ij}^e} - \frac{N_i}{D_{i,k}^e} = \frac{P}{RT} \frac{\delta x_i}{\delta r} + \frac{x_i}{RT} \left( \frac{B_0 P}{\mu D_{i,k}^e} + 1 \right) \frac{\delta P}{\delta r}$
$D_{i,k}^e = \frac{4}{3} K_0 \sqrt{\frac{8RT}{\pi M_i}} \quad (\text{Knudsen diffusion coefficients})$
$D_{ij}^e = \frac{\varepsilon}{\tau} D_{ij}^0 \quad (\text{Bulk diffusion coefficients})$
Boundary conditions:
Fixed conditions at membrane interfaces (Dirichlet type):
$t = 0 \quad p_i(0, r) = \Pi_i(r) \quad \forall r, i = 1, \dots, n$
$r = r_t \quad p_i(t, r_t) = p_i(0) \quad \forall t, i = 1, \dots, n$
$r = r_s \quad p_i(t, r_s) = p_i(0) \quad \forall t, i = 1, \dots, n$
Equal internal and external mole fluxes at membrane interfaces:
(a) Negligible convective flows (von Neumann type):
$t = 0 \quad p_i(0, r) = \Pi_i(r) \quad \forall r, i = 1, \dots, n$
$r = r_t \quad (k_{gi})_t \cdot [x_i(t, r_t) - \langle x_i \rangle_t] P / RT = N_i(t, r_t) \quad \forall t, i = 1, \dots, n$
$r = r_s \quad (k_{gi})_s \cdot [\langle x_i \rangle_s - x_i(t, r_s)] P / RT = N_i(t, r_s) \quad \forall t, i = 1, \dots, n$
(b) Relevant convective flows:
$t = 0 \quad p_i(0, r) = \Pi_i(r) \quad \forall r, i = 1, \dots, n$
$r = r_t \quad 1 + \frac{x_i(t, r_t) - \langle x_i \rangle_t}{[N_i(t, r_t) / \sum_{j=1}^n N_j(t, r_t)] - x_i(t, r_t)} = \exp\left(\frac{-RT \sum_{j=1}^n N_j(t, r_t)}{P(k_{gi})_t}\right) \quad \forall t, i = 1, \dots, n$
$r = r_s \quad 1 + \frac{x_i(t, r_s) - \langle x_i \rangle_s}{[N_i(t, r_s) / \sum_{j=1}^n N_j(t, r_s)] - x_i(t, r_s)} = \exp\left(\frac{RT \sum_{j=1}^n N_j(t, r_s)}{P(k_{gi})_s}\right) \quad \forall t, i = 1, \dots, n$

in Fig. 1). The expressions for the calculation of the above coefficients in our case are:

$$(k_{gi})_t = 1.73 \frac{D_i^0}{r_t - r_{\text{oil}}} \quad (2)$$

$$(k_{gi})_s = 2.63 \frac{D_i^0}{r_{\text{shell}} - r_s} \quad (3)$$

Concerning the transport equations, three parameters, namely  $K_0$ ,  $B_0$ , and  $\varepsilon/\tau$ , need to be known *a priori*, and must be measured independently via preliminary characterisation routes.

$\varepsilon/\tau$  was esteemed with specific reactive runs, as described in paper I (Saracco *et al.*, 1995), obtaining a value of 0.097 and 0.124 for model D and model E, respectively, whereas  $K_0$  and  $B_0$  need to be determined via specific characterisation procedures. These two parameters are related to the Knudsen component of the diffusive flow and to the d'Arcy expression

of the convective flow, and can be measured through simple permeation runs with pure inert gases. In this case, at steady-state conditions and in the absence of reaction, the flux expression in Table 1 reduces to

$$N_i = -\frac{1}{RT} \left( \frac{B_0 P}{\mu} + \frac{4}{3} K_0 \sqrt{\frac{8RT}{\pi M_i}} \right) \frac{dP}{dr} \quad (4)$$

Assuming that the physical parameters are constant over the tubular membrane, expression (4) becomes, after substitution in the overall mass balance and integration (the generic component  $i$  is assumed to be fed at the tube side):

$$N_{i,t} = \frac{1}{RT} \left( \frac{B_0}{\mu} \frac{P_t + P_s}{2} + \frac{4}{3} K_0 \sqrt{\frac{8RT}{\pi M_i}} \right) \frac{P_t - P_s}{r_t \ln(r_s/r_t)} \quad (5)$$

Varying  $N_{i,t}$ ,  $P_t$  and  $P_s$ , estimates of  $K_0$  and  $B_0$  can be easily obtained (Section 4), once  $\mu$  is evaluated with

a suitable method. The method by Chung *et al.* was used for this purpose in the present study (Reid *et al.*, 1987).

Finally, as concerns the reaction rate, literature on propane catalytic combustion on Pt/Al<sub>2</sub>O<sub>3</sub> catalysts (Moro-oka *et al.*, 1967; Hiam *et al.*, 1968) demonstrates that, over a wide range of concentrations, a power law expression is followed with reaction orders for propane and oxygen equal to 1 and 0, respectively. Assuming an Arrhenius-type expression for the kinetic constant the following equation is obtained:

$$\mathcal{R}_{\text{C}_3\text{H}_8} = K' \exp\left(-\frac{E_a}{RT}\right) \frac{p_{\text{C}_3\text{H}_8}}{RT}. \quad (6)$$

$E_a$  was measured as  $7.37 \times 10^4 \text{ J mol}^{-1}$  in the above quoted references. The pre-exponential constant  $K'$  can be evaluated as a fitting parameter, using either model D or model E, taking into account only the experimental results concerning the kinetics-controlled operating regime (i.e. low conversions).

### 3. THE EXPERIMENTAL SETUP

A complete description of the experimental setup was given in Saracco *et al.* (1995), where details about the preparation and the basic characterisation of the catalytic membrane were also reported.

Briefly, the reactor is a shell-and-tube module housing a tubular catalytic membrane (see Fig. 1:  $L = 100 \text{ mm}$ ;  $r_t = 7 \text{ mm}$ ;  $r_s = 10 \text{ mm}$ ;  $r_{\text{shell}} = 25 \text{ mm}$ ;  $r_p = 3.5 \mu\text{m}$ ;  $\gamma\text{-Al}_2\text{O}_3$  content = 4% b.w.; Pt content = 1% b.w. referred to the  $\gamma\text{-Al}_2\text{O}_3$ ), whose temperature, measured by a K-type thermocouple touching its external surface in the middle of the membrane length, is controlled by means of a PID-regulated oven in which the entire reactor is contained. The temperature of the shell of the module and of the oil pipe, placed for heat removal purposes at the tube side of the membrane, were monitored as well. The feed flow rates of a propane–nitrogen mixture and of air are fed countercurrently to their respective chambers by means of mass flow meters. The pressures at the

tube or at the shell side of the membrane are controlled via back-pressure regulators placed close to the chamber outlets. Chemical analysis of the inlet and outlet flow rates was performed by IR spectrometry (CO<sub>2</sub>) and gas chromatography (C<sub>3</sub>H<sub>8</sub>, O<sub>2</sub>, H<sub>2</sub>O). The flow rates were also measured by gas-chromatographic analysis, dosing SF<sub>6</sub> as a tracer at a known flow rate. By these means overall mass balances could be verified with deviations less than 15%.

### 4. MEMBRANE CHARACTERISATION

Permeation experiments on the activated membrane were performed with both N<sub>2</sub> and He. A constant gas flow rate was imposed through the membrane using the tube side of the module as the inlet side (equivalent results can be obtained feeding the permeating gas at the shell side). The resulting pressure difference over the membrane was recorded as a function of the outlet pressure.

Equation (5) can be rearranged into

$$\frac{\phi P_t \ln(r_s/r_t)}{2\pi L(P_t - P_s)} = \frac{B_0}{\mu} \frac{P_t + P_s}{2} + \frac{4}{3} K_0 \sqrt{\frac{8RT}{\pi M_i}}. \quad (7)$$

Figure 2 reports the results of the permeation runs plotting the first member of eq. (7) as a function of the average pressure inside the membrane. The obtained  $K_0$  and  $B_0$  values are summarised in Table 2. The average values will be used in model calculations.

On the other hand, for the estimation of the pre-exponential rate constant  $K'$  a number of runs were performed in the absence of any pressure difference across the membrane, and feeding a propane–nitrogen mixture either at the shell- or the tube-side of the module and pure air at the opposite side. Inlet flow rates were kept equal to  $2 \text{ Nl min}^{-1}$  for both gas mixtures. The propane concentration in the feed was varied between 2 and 18.6%. The temperature of the shell of the module,  $T_{\text{shell}}$ , was increased from about 100°C to about 500°C to achieve progressively higher conversion levels.  $K'$  values were derived by fitting the

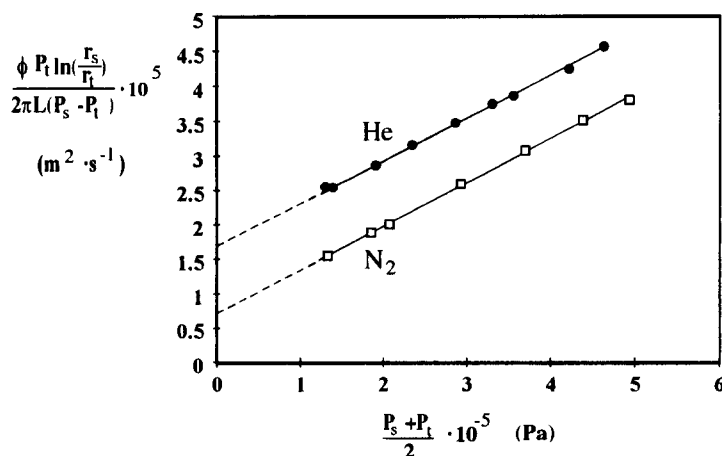


Fig. 2. Results of permeation runs.

Table 2. Results of permeation runs

	$K_0 \times 10^9$ (m)	$B_0 \times 10^{16}$ (m <sup>2</sup> )
He	7.56	7.38
N <sub>2</sub>	8.01	6.85
Average	7.78	7.11

experimental conversion data with either model D or E as a function of the surface membrane temperature  $T_m$ , considering only the kinetics-controlled regime until the overall conversion remained lower than about 10% of the maximum attainable conversion (e.g. infinitely fast kinetics). Figure 3 shows the behaviour of the reactor in the above-underlined temperature range. Steady-state multiplicity can be noticed (i.e. the ignition and the extinction shell temperatures are somewhat different from each other). This phenomenon, likely determined by heat transfer towards heat exchange surfaces (i.e. oil pipe, module shell), widens, in a way, the margins for operation in the transport-controlled regime. In fact, once the reactor is ignited, it can operate even below the ignition shell temperature.

On the other hand, during  $K'$  determination runs in the kinetics-controlled regime, slip of reactant was noticeable. However, due to the comparatively high flow rates passing through the chambers, the concentration of the slipped reactants remained always lower than 1% of the concentration in the respective feed chamber. Under these conditions any limitation of the reaction rate due to absence of oxygen in some part of the membrane was avoided. Moreover, due to the first-order dependence of the reaction rate on propane concentration [see eq. (6)], the derived kinetic constants have to be considered as an index of the catalytic activity of the membrane at the side exposed to the highest propane concentrations (i.e. the feed side of propane).

The results are plotted in Fig. 4 for either model D or E and for both feed sides. Some remarks must be presented to the merits. First, the system seems to be asymmetric with respect to its catalytic activity: the tube side of the membrane seems to be more active than the shell side. This can be due to the migration of Pt and/or of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> precursors during the drying steps of their deposition procedures. Second, the two models give slightly different estimates of  $K'$ . Once again in model D the effect of the external mass transfer resistance, which is not considered directly, is partially lumped into the  $K'$  value. The observed differences are though small, likely because the effect of the external mass transfer was already included in the  $\varepsilon/\tau$  value, as discussed in paper I (Saracco *et al.*, 1995).

Further, it is evident  $K'$  that decreases with increasing the propane feed concentration. This may be due to a slight overestimation of the reaction order for the propane, or to a certain temperature dependence of  $K'$ .

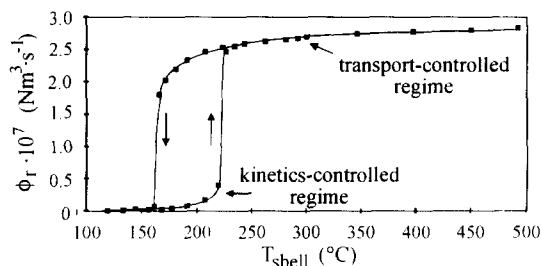


Fig. 3. Reactor performance in the transition zone between the kinetics- and the transport-controlled regimes (propane feed concentration: 6.3%; feed side: shell).

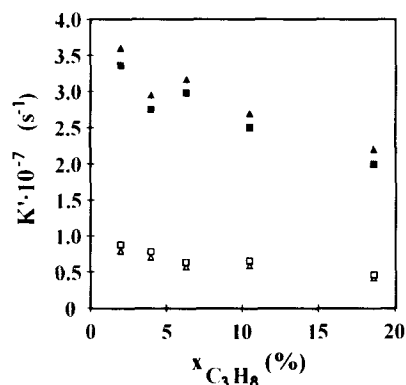


Fig. 4. Obtained values of the pre-exponential kinetic constant  $K'$  as a function of propane concentration. Model D: ( $\blacktriangle$ ,  $\triangle$ ) tube, shell side; model E: ( $\blacksquare$ ,  $\square$ ) tube, shell side.

Some final remarks have to be addressed to the determination of the membrane surface temperature  $T_m$ . A number of issues make the reliability of this measurement questionable (the contact between the thermocouple and the membrane surface takes place in a single point; the gas flowing in the shell chamber may actually supply/remove heat to/from the tip of the thermocouple; heat conduction along the thermocouple itself may affect the measurement). The above effects however should be negligible whenever  $T_m$  and  $T_{shell}$  are close to each other (i.e. there are no severe radial temperature gradients in the shell chamber). This is the case of the kinetics-controlled regime in which the difference between the two above temperatures was always lower than 20°C. Once the reactor is ignited the gap between  $T_m$  and  $T_{shell}$  may become relevant (> 50°C). Though, in this case, conversion is limited by mass transfer and any heat transfer effect should be of minor importance, since diffusion coefficients are by far less temperature-sensitive than kinetic constants. Typical activation energies for diffusive phenomena might be as low as 40–60 kJ mol<sup>-1</sup>, while heterogeneously catalysed reactions generally have activation energies higher than 120 kJ mol<sup>-1</sup> (Satterfield, 1991). This means that eventual uncertainties in the measurement of  $T_m$  and possible temperature gradients inside the membrane, not taken into account in the isothermal modelling employed, should

not affect in a marked way the accordance of the above modelling with the experimental reactor performance.

### 5. RESULTS OF REACTIVE RUNS

The major aim of this study is to describe the performance of the reactor in the transport-controlled regime when pressure gradients are applied across the membrane. For such a purpose in a series runs the effect of such gradients on the overall per pass conversion was studied. In all runs  $T_{\text{shell}}$  and the feed flow rates were kept equal to 490°C and 2 Nl min<sup>-1</sup>, respectively. The lower-pressure chamber was always kept at 2 bar.

Figure 5 shows, for both tube-feed and shell-feed of propane, the conversion attained with a 7% C<sub>3</sub>H<sub>8</sub> feed concentration. By convention, pressure differences were calculated subtracting the pressure at the air side to that at the propane side. In the same figure the predictions of both isothermal models D and E (Table 1) are also reported. The superscript + refers, for given boundary conditions, to the use of the higher pre-exponential kinetic constant measured (tube side), the superscript - to the lower one (shell side, see Fig. 4).

The conversions measured in the same pressure-difference range with a 4% and 7% propane-N<sub>2</sub> gas feed are reported together in Fig. 6 for a comparison. Finally, Fig. 7 plots the variation of the slip fraction  $S_{\text{C}_3\text{H}_8}$ , defined as follows:

$$S_{\text{C}_3\text{H}_8} = \frac{r_s N_A(r_s)}{r_t N_A(r_t)} \quad (8)$$

as a function of the applied pressure difference during the same runs.

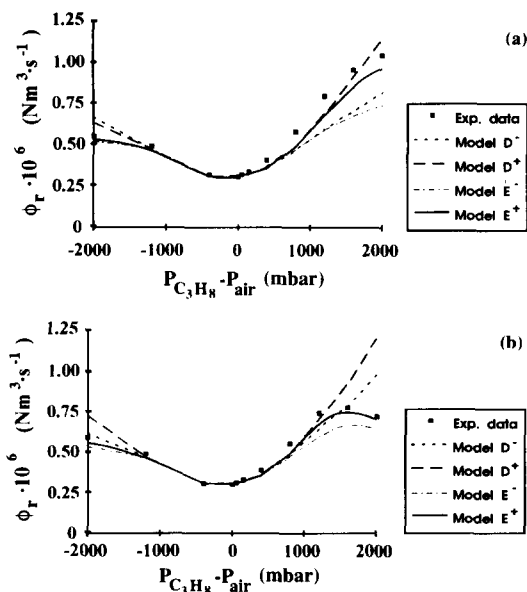


Fig. 5. Accordance of the isothermal models D and E with experimental conversion data at varying the pressure difference imposed over the membrane for both shell-feed (a) and tube-feed (b) of propane. (+) higher  $K'$  values used; (—) lower  $K'$  values used (see Fig. 3).

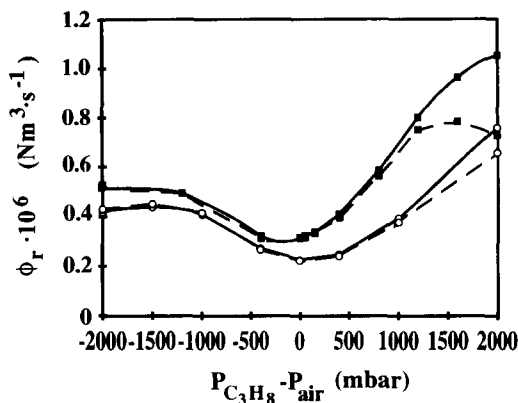


Fig. 6. Effect of pressure difference applied over the membrane on the converted flow rate for two different propane feed concentrations ( $\circ$  = 4%;  $\blacksquare$  = 7%) and for both shell (—) and tube (---) feed of propane.

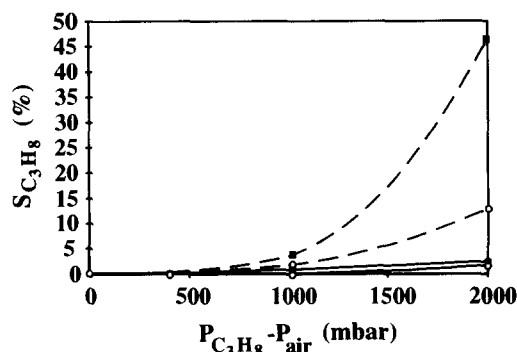


Fig. 7. Effect of the pressure difference applied over the membrane on the propane slip fraction. Same operating conditions and notations used in Fig. 6.

### 6. DISCUSSION

It clearly appears from the data plotted in Fig. 5, how the application of a pressure difference can significantly increase conversion (up to 300%) if either air or propane are fed at the low pressure chamber. The reason for this is clear. Provided kinetics are high enough, the reaction zone is shifted towards the low-pressure side where the concentration gradient of the species that moves against the convective flow becomes steeper, allowing higher diffusive fluxes, and, consequently, higher conversions. Nonetheless, a limit to this increase is met for two main reasons:

- Above certain convective flow rates (i.e. pressure differences) it is technically difficult to enhance kinetics so as to maintain the reaction zone inside the membrane, and to avoid slip of reactants.
- When the convective flow through the membrane is increased the interfacial concentration of the component which moves against the pressure gradient is decreased compared to the bulk concentration of the gas mixture, due to external

mass transfer resistance, until it becomes practically zero. In these conditions the diffusive flux is completely controlled by the external mass transfer resistance and it is proportional to the bulk concentration in the low pressure chamber. Moreover this bulk concentration decreases when the applied pressure difference is enhanced, because of the increasing amount of inert gas coming in the low pressure chamber.

As a consequence of these observations it is easy to understand why model E gives generally more accurate predictions of the reactor performance than model D, which does not account for the external mass transfer resistance, and, therefore, overestimates conversion when high pressure differences are applied. Particularly, model E can correctly predict the maximum-in-conversion observed during the series runs performed with a tube-side feed of propane [Fig. 5(a)]. This maximum was not observed when feeding propane at the shell side because in this case the reaction plane tends to move towards the more active tube-side of the membrane.

A further issue concerning this topic is the tendency of model E to slightly underestimate the attained conversion at high pressure differences. This is more evident when propane rather than air is pushed through the membrane. A particular mechanism may be proposed to explain these results: additional conversion of slipped reactants in dead-end pores at the membrane surface (Fig. 8).

Since now, every modellistic approach that aims at the simulation of the reactor performance has been based on the assumption that the reaction could take place only in the activated pores passing through the membrane and permeated from opposite sides by the two reactants. However, as represented in Fig. 8, due to imperfect distribution of the catalytically active phase some pores would probably result obstructed after the activation route. SEM observations proved

the existence of this phenomenon. These dead-end pores can be permeated only from one side of the membrane. When a reactant (propane in Fig. 8) slips through the membrane, it can be driven to the entry of a dead-end pore, and permeate together with the other reactant, thus enabling additional conversion.

Slip of propane becomes relevant above certain pressure differences (Fig. 7). It might enable reaction in dead-end pores and gives further conversion which is not accounted for by the model. Moreover if equal slip amounts of propane and oxygen are considered to pass through the membrane, the former is potentially capable of generating a five times higher additional conversion than the latter, as a consequence of reaction stoichiometry. This may explain the different behaviour of the reactor compared to the model estimates when propane is fed at the high pressure chamber, or at the low pressure one.

In principle, the above mechanism might be included in the model by including differential mass balances along the membrane length in the system of equations to be solved. However, two main issues would likely render this action inconvenient:

- the computational time required would markedly increase;
- the determination of the actual number of dead-end pores available would be quite problematical.

Moreover, other phenomena may also contribute to the above conversion increase. For instance, it may be possible that the measured  $T_m$  values, based on which model E predictions were evaluated, are somewhat lower than the actual membrane temperature, owing to the above discussed heat effects which disturb the measure of the thermocouple. Further, localised temperature variations across and along the membrane, not measured by the single thermocouple, might play a role in this context.

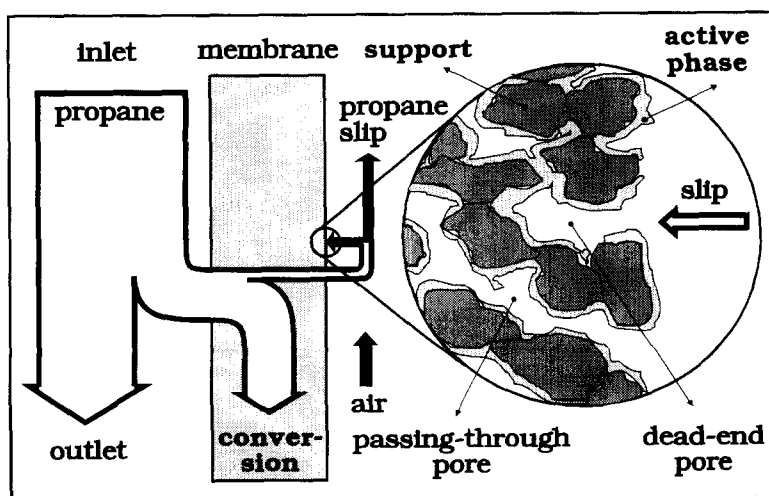


Fig. 8. The mechanism of additional conversion in dead-end pores.



Finally, Fig. 6 shows how the maximum-in-conversion is not attained, in the investigation range of pressure differences, when pushing a 4% propane gas feed into the membrane from either the tube or the shell side. Contrary to the 7% propane feed, the maximum-in-conversion is registered when pushing air through the membrane. When propane is fed in stoichiometric excess (e.g. 7%), the reaction zone shifts towards the air side and any additional convective flow increasing the trans-membrane flux of propane renders the location of this zone more and more critical with respect to the above-described mechanisms of conversion limitation due to the external mass transfer resistance. When propane is fed at a lower concentration (e.g. 4%) the reaction zone tends to stand closer to the feed-side. It is then more difficult to "blow" this zone out of the air-side of the membrane by the application of a pressure difference. Conversely, when a convective flow of air is forced into the membrane, it becomes easier to reach conditions for a limitation in conversion.

## 7. CONCLUSIONS

The application of a pressure difference over the membrane was demonstrated to be an effective mean to increase conversion (up to about 300%) in a membrane reactor with separate feed of reactants, without losing, within certain limits, its interesting properties (see Section 1).

Two models, named D and E, which respectively neglect or consider the external mass transfer resistance have been presented and numerically solved obtaining good accordance with the experimental propane conversion measured as a function of the applied pressure difference over the membrane.

For high pressure differences ( $> 1$  bar) the use of model E appears to be a *conditio sine qua non*, since model D overestimates conversion unacceptably. The choice between the two modelling approaches is though not trivial at lower pressure differences. Model E is fundamentally more correct but its numerical solution is also more complicated and time-consuming than that of model D, so this last one should be preferred whenever its predictions remain sufficiently accurate (limited pressure differences over the membrane). However, in the absence of suitable criteria model E should always be used for a check.

On the basis of the above evidence, it can be concluded that the potentiality of success of the considered reactor setup appears to be wider when pressure gradients are applied across the membrane compared to what was concluded in paper I (Saracco *et al.*, 1995), in which the effect of only diffusive mass transfer through the membrane was studied.

As a final consideration it has to be once again underlined how the obtained results are strictly linked to the structural and kinetic parameters of the membrane employed in this study. Even more attractive results for practical application might be obtained

with a membrane having different permeability or catalytic activity. An optimisation is necessary. A primary role should be played in this context by the presented models.

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## NOTATIONS

$B_0$	permeation constant, $\text{m}^2$
$D$	diffusion coefficient, $\text{m}^2 \text{s}^{-1}$
$E_a$	apparent activation energy, $\text{kJ mol}^{-1}$
$k_g$	mass transfer coefficient, $\text{m s}^{-1}$
$K'$	pre-exponential kinetic constant, $\text{s}^{-1}$
$K_0$	Knudsen constant, m
$L$	membrane thickness, m
$M$	molecular mass, $\text{kg mol}^{-1}$
$n$	number of components
$N$	mole flux, $\text{mol m}^{-2} \text{s}^{-1}$
$p$	partial pressure, Pa
$P$	absolute pressure, Pa
$r$	radius, m
$R$	universal gas constant ( $= 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ )
$\mathcal{R}$	reaction term, $\text{mol m}^{-3} \text{s}^{-1}$
$S$	slip fraction
$t$	time, s
$T$	temperature K
$x$	mole fraction
$\langle x \rangle$	mixing-cup mole fraction

## Greek letters

$\varepsilon$	porosity
$\phi$	volumetric flow rate, $\text{N m}^3 \text{s}^{-1}$
$\mu$	viscosity, Pa s
$\nu$	stoichiometric coefficient
$\Pi$	assigned partial pressure value, Pa
$\tau$	tortuosity

## Subscripts

$A, B, C,$	generic components
$i, j$	
$k$	Knudsen
$m$	membrane
oil	oil pipe
$p$	pore
$s, t$	shell-, tube-side of the membrane
shell	shell of the reactor module

## Superscripts

$e$	effective
$o$	gas-phase

## REFERENCES

- Bird, R. B., Stewart, W. E. and Lightfoot, E. N., 1960, *Transport Phenomena*. Wiley, New York.
- Hiam, L., Wise, H. and Chaikin, S., 1968, Catalytic oxidation of hydrocarbons on platinum. *J. Catalysis* **9–10**, 272–276.

- Lundberg, R. E., McCuen, P. A. and Reynolds, W. C., 1963, Heat transfer in annular passages. Hydrodynamically developed laminar flow with arbitrarily prescribed wall temperatures or heat fluxes. *Int. J. Heat Mass Transfer*, **6**, 459–529.
- Mason, E. A. and Malinauskas, A. P., 1983, *Gas Transport in Porous Media: the Dusty-Gas-Model*, Chemical Engineering Monographs, Vol. 17. Elsevier, Amsterdam.
- Moro-oka, Y., Morikawa, Y. and Ozaki, A., 1967, Regularity in the catalytic properties of metal oxides in hydrocarbon oxidation. *J. Catalysis* **7**, 23–32.
- Reid, R. C., Prausnitz, J. M. and Poling, B. E., 1987, *The Properties of Gases and Liquids*, 4th Edition. McGraw-Hill, New York.
- Saracco, G., Veldsink, J. W., Versteeg, G. and van Swaaij, W. P. M., 1995, Catalytic combustion of propane in a membrane reactor with separate feed of reactants. I. Operation in absence of trans-membrane pressure gradients, paper 1 of this series. *Chem. Engng Sci.* **50**, 12, 2005–2015.
- Satterfield, 1991, *Heterogeneous Catalysis in Industrial Practice*, 2nd Edition. McGraw-Hill, New York.
- Veldsink, J. W., 1993, A catalytically active, non-permselective membrane reactor for kinetically fast, strongly exothermic heterogeneous reactions. Ph.D. dissertation, University of Twente, The Netherlands.
- Veldsink, J. W., van Damme, R. M. J., Versteeg, G. F. and van Swaaij, W. P. M., 1992, A catalytically active membrane reactor for fast, heterogeneously catalysed reactions. *Chem. Engng Sci.* **47**, 9–11, 2939–2944.