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MEMBRANE REACTOR FOR WATER DETRITIATION: A PARAMETRIC STUDY ON OPERATING PARAMETERS

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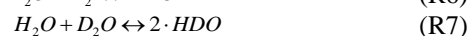
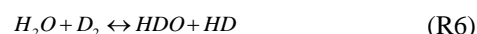
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This paper presents the results of a parametric study done on a single stage finger-type packed-bed membrane reactor (PBMR) used for heavy water vapor dedeuteration. Thanks to mass spectrometer analysis of streams leaving the PBMR, speciation of deuterated species was achieved. Measurement of the amounts of each molecular component allowed the calculation of reaction quotient at the packed-bed outlet (i.e. retentate). They highlighted that isotopic exchange reactions occurring on the catalyst particles surface are not thermodynamically equilibrated. Moreover, variation of the heavy water content in the feed exhibits competition between permeation and conversion kinetics.

I. INTRODUCTION

During its lifecycle, a D-T fusion machine will produce amounts of tritiated waste of various activities and natures. Several issues associated to tritiated waste management have been pointed out since 1997 as a result of the DTE1 experiments done in the JET machine.¹ Thus, for economic and ecological reasons, several processes have been developed since decades either to trap volatile tritiated species (Q_2 and/or Q_2O) by oxidation/ad(ab)sorption processes or to recover them as fusion fuel.²

A promising process considered for recycling these waste products uses combined effects of catalytic conversion and selective membrane purification properties. Even though efficiency of such a process has already been demonstrated either on soft housekeeping waste³ or highly tritiated water effluents,⁴ some mechanisms, particularly in terms of reaction conversions are not really well known yet. Considering deuterium as tritium tracer, the overall set of reactions occurring with a Q_2/Q_2O mixture is given below:



From the above reversible reaction set, two possible chemical pathways appear: if reactions' thermodynamic equilibriums are reached, R1 to R3 reactions are sufficient to describe the whole system. Indeed, R4 to R7 equilibrium constants are linear combinations of the three others. Nevertheless, if chemical reacting system is rate limited, kinetics of each of the 7 reactions must be considered. The following sensitivity analysis will be used to identify pathway that must be considered in the catalytic membrane reactor modeling.

II. EXPERIMENTAL APPARATUS

An experimental test bench has been built at CEA Cadarache to realize parametric study on catalytic membrane reactors. Figure 1 gives a schematic view of the instrumented experimental device; a detailed description of the process has already been reported (Ref. 5). Briefly, diluted deuterated feed stream, composed of binary mixtures of N_2 and D_2O , is fed to the lumen side of a finger-type PBMR containing about 20 grams commercial Ni-Based catalyst pellets (NiSAT[®] 310RS CDS). The membrane tube (length = 48.5 cm, outer diameter = 1 cm, wall thickness = 150 μ m) is made of a defect free $Pd_{77}Ag_{23}$ alloy allowing hydrogen isotopes permeation exclusively. The feed stream reacts with permeated protium brought by the counter-current sweep stream. Deuterium hydride and dideuterium produced are partially removed from the lumen side by counter-diffusion through the membrane and withdrawn by the permeate stream. Remaining reaction products are removed by the retentate stream.

While feed composition is adjusted by species injection flow rate control, retentate and permeate ones are measured by a Hiden[®] HAL201RC quadrupole mass spectrometer (QMS). As shown on Fig. 1, the sampling system is made of small diameter heated tubes in order to minimize hold-up and wall adsorption effects. Tube diameter has been designed to maintain viscous flow

regime in the sampling line and avoid segregation phenomenon of the sample. The sampling flow, ensured by a primary vacuum pump, is controlled to minimize residence time of the gas in the tube. Injection of the gas sample in the ionization chamber of the QMS is done by effusion through calibrated holes (leak-type injector). Before switching the analysis from one stream to the other, sampling line is baked and flushed with nitrogen to degas remaining species.

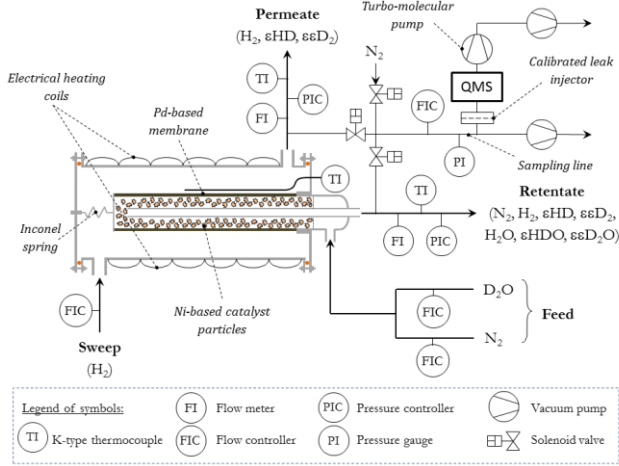


Fig. 1. Scheme of the test bench

Calibration of the analysis chain was done with in-house standards of diluted binary and ternary mixtures of Q₂ and Q₂O at different pressure and sampling flow rate. Correlation between intensity of the parent ion peak and absolute amounts of corresponding molecule (e.g. m/z=20 for D₂O) have been established. At the same time, abundances of fragments produced during the ionization process were related to the parent ion peak intensity; good agreements with the NIST mass spectrums databanks⁶ were found. Thanks to these procedure, contribution of heavy molecules fragments can be removed during the determination of Q₂ amounts in the gas sample (e.g. Q₂O fragments measured at m/z=2 and/or 3 were subtracted during the calculation of Q₂ amount in the retentate).

Combining these composition results with those of streams total flow rates allowed to track molecular and atomic species from any inlets to any outlets of the catalytic membrane reactor. As a result, data reconciliation on gross measurements results could be done. During this post-treatment step, new sets of experimental results, respecting atomic balance of the system, were calculated. On the 73 assays done during this sensitivity study, a maximal deviation of 7% was encountered between gross and reconciled measurements.

III. SENSITIVITY ANALYSIS RESULTS

Parametric studies, whose results are presented below, have been done on 3 operating parameters which are: the membrane temperature, the total feed flow rate

and the feed composition through D₂O content variations. The catalytic membrane reactor response to these parameter perturbations have been quantified in terms of:

- Decontamination factor (DF) defined as deuterium feed to retentate output ratio

$$DF = \frac{2 \cdot (y_{D_2, feed} + y_{D_2O, feed}) \cdot \dot{N}_{feed}}{[y_{HD, ret} + y_{HDO, ret} + 2 \cdot (y_{D_2, ret} + y_{D_2O, ret})] \cdot \dot{N}_{ret}} \quad (1)$$

With $y_{i,j}$ the molar content of specie i in the j -stream and \dot{N}_j its molar flow rate in mol.s⁻¹

- Relative deuterium repartition F_i^j as a function of the molecular form of the deuterium containing i -specie in the j -stream

$$F_{H_{n-2}D_nO_m}^j = \frac{n \cdot y_{H_{n-2}D_nO_m, j} \cdot \dot{N}_j}{2 \cdot (y_{D_2, feed} + y_{D_2O, feed}) \cdot \dot{N}_{feed}} \quad (2)$$

With n and m the respective numbers of deuterium and oxygen atoms in the molecule

- r -reaction quotient to equilibrium constant ratio EG_r ; it quantifies the gap between actual species distribution and the one they should have with respect to thermodynamic equilibrium state. According to the mass action law, and considering that, due to the low pressures involved in this study (i.e. up to 3 absolute bar), gas phase behavior can be modeled by ideal gas equation of state, it can be written as:

$$EG_r = \frac{\prod_i P_i^{v_{i,j}}}{K_r} \quad (3)$$

Where K_r stands for the equilibrium constant of the r -reaction at membrane temperature, $v_{i,j}$ the stoichiometric coefficient of the i -specie in the r -reaction

During all the experiments, swamping H₂ to D₂O flow rate ratio was maintained at 100:1 in order to maximize the PBMR efficiency. Indeed, in their light water deuteration experiments done on the PERMCAT process, Demange and coworkers highlight a linear dependency of the decontamination factor with this ratio.⁷ For the same reason, transmembrane pressure difference had been maximized, setting retentate and permeate pressures respectively to 2.7 bar and 0.5 bar.

III.A. Temperature and Feed Flow Rate Variations

Fluctuations of membrane temperature have been done by modification of the electrical current supplied to the external heating coils. Figure 2 shows the evolution of decontamination factor as a function of the temperature for three different feed flow rates.

It appears that DF follows a rather linear tendency. An average increase of 25% appears on the 3 flow rates in the range of 320 °C to 400 °C. It can be attributed to the enhancement of permeation flux. Indeed, considering that

Richardson's law is applicable, the permeable i -specie transmembrane flux in a cylindrical membrane is expressed as:

$$J_i = \phi_i \cdot \frac{\pi \cdot L}{\ln(r_{in}/r_{out})} \cdot (\sqrt{P_{i_2,ret}} - \sqrt{P_{i_2,perm}}) \quad \forall_i \in [H, D] \quad (4)$$

With L the membrane length, r_{in} and r_{out} respectively the inner and outer membrane radius and ϕ_i the i -specie membrane permeability.

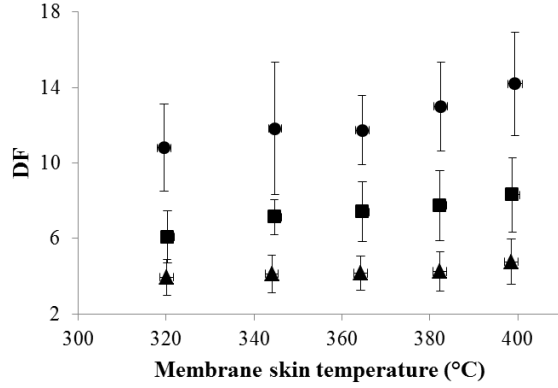


Fig. 2. DF versus membrane temperature for feed flow rates of ● 100 mL(STP) min⁻¹, ■ 200 mL(STP).min⁻¹ and ▲ 300 mL(STP).min⁻¹ and D₂O molar content in the feed of 1 mol.% in N₂

According to the measurements done in a previous work,⁵ the membrane permeability increase (rather linear in this range of temperature) is about 30%. Thermal increase of the DF is thus due to the enhancement of the deuterated reaction products withdrawal.

On the contrary, increasing the feed flow rate reduces the DF. Indeed, Table I shows an increase in both unreacted HDO and D₂O and deuterated products HD and D₂ in the retentate stream. It means that, on one hand, pollutants conversion is reduced due to the decrease of their contact time with catalyst's active sites and, on the other hand, reaction products do not have enough time reach the membrane surface and permeate.

This last phenomenon could have two possible reasons:

- the membrane surface dissociative adsorption of Q₂ species is kinetically controlled ; thus, when characteristic adsorption time become larger than advection one, molecular Q₂ species are directly swept to the retentate stream. Such a limitation is in contradiction with the hypothesis of the Richardson's law applicability and had not been highlighted in the previous membrane characterization study.⁵
- the more promising justification deals with reaction peak displacement. This one, corresponding to the fixed bed area in which species generation/consumption are the most important, could be shifted closer to the packed bed outlet as the feed flow rate increase. As a consequence, reaction

products are created further and the remaining membrane surface area is not sufficient to evacuate them to the shell side.

Validity of this hypothesis will be checked in a forthcoming modeling study.

TABLE I. Relative Deuterium Repartition for Membrane Temperature of 320°C and D₂O Molar Content in the Feed of 1 mol.% in N₂

	$\dot{V}_{feed} = 100 \text{ mL(STP) min}^{-1}$	$\dot{V}_{feed} = 200 \text{ mL(STP) min}^{-1}$	$\dot{V}_{feed} = 300 \text{ mL(STP) min}^{-1}$
F_{HD}^{ret}	4.1% ± 1.3%	10.0% ± 2.8%	18.1% ± 5.2%
$F_{D_2}^{ret}$	0.02% ± 0.01%	0.09% ± 0.02%	0.23% ± 0.03%
F_{HDO}^{ret}	1.4% ± 0.2%	2.1% ± 0.4%	3.0% ± 0.4%
$F_{D_2O}^{ret}$	0.8% ± 0.2%	0.80% ± 0.2%	0.8% ± 0.2%
F_{HD}^{perm}	64.6% ± 2.8%	60.1% ± 3.9%	54.4% ± 5.7%
$F_{D_2}^{perm}$	29.3% ± 2.3%	23.9% ± 1.9%	21.7% ± 1.8%

All the margins of errors are presented at 95% confidence interval.

III.B. D₂O Feed Content Variation

Variations of D₂O content in the feed stream have been performed at constant overall feed flow rate. Figure 3 highlights an optimal value of pollutant content for which the decontamination factor exhibits a maximum value. Below this value, DF increases with D₂O content; it seems to be due to the fact that the increase of the reagent concentration speeds up species net conversions. Indeed, due to the high H₂ to D₂O flow rate ratio, heavy water vapor acts as a limiting reagent; reaction rates highly depend on its concentration in the reacting mixture. As a result, increasing of the D₂O amount in the feed enhance the deuterated water vapor to light water vapor conversion ratio.

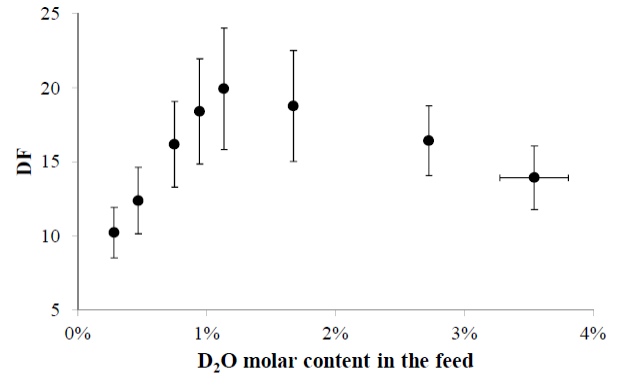


Fig. 3. DF values versus D₂O molar content in the feed for membrane temperature of 320 °C and feed flow rate of 100 mL(STP).min⁻¹

Beyond this optimal value, the decontamination factor decrease can be related to the membrane area

limitation. Indeed, increasing D_2O amount produces more Q_2 reaction products. As shown by Eq. (4), transmembrane flux will also increase as a consequence of the Q_2 partial pressure rise in the retentate. But, as the membrane area is limited, transmembrane flow rate will not be sufficient to withdraw HD and D_2 products; they will be recovered in the retentate stream. Moreover, as shown on Fig.4, this phenomenon also limits the shift effect. The composition of the retentate mixture is getting closer to the one obtained under thermodynamic equilibriums conditions as the D_2O content in the feed increase.

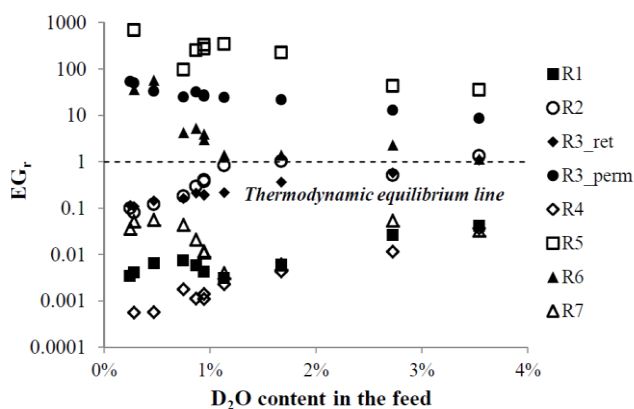


Fig. 4. Reaction quotient to equilibrium ratio versus D_2O molar content in the feed for membrane temperature of $320\text{ }^\circ\text{C}$ and feed flow rate of $100\text{ mL(STP) min}^{-1}$

In addition, one can see on the above figure that no one of the seven considered reactions have reached their thermodynamic equilibrium state: five of them evolve in the direct way ($EG_r < 1$) while the others follow the reverse one.

This non-equilibrium state assessment meets Demange and co-workers observations.^{6,7} Indeed, they reported enhanced PERMCAT process performances with higher catalyst mass to permeation area ratio. The residence time increase helps reacting mixture to reach higher conversion ratios.

IV. CONCLUSIONS

A sensitivity study was done on the main operating parameters of a PBMR. While temperature variation mainly influences permeation efficiency, feed flow rate perturbation reveals dependence of conversion and permeation properties to contact time between catalyst and reacting mixture. Moreover, parametric study done on feed composition shows that an increase in D_2O content leads to an enhancement of heavy water vapor to light water vapor conversion. It highlights the fact that chemical system is not under thermodynamic equilibrium.

Nevertheless, due to the strong couplings between the various phenomena occurring in the PBMR (i.e. mass, thermal and momentum transfers, reaction kinetics ...), a phenomenological modeling is needed to go further in the results interpretation.

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