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MODELING AND DATA ANALYSIS OF A PALLADIUM MEMBRANE REACTOR FOR TRITIATED IMPURITIES CLEANUP

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INTRODUCTION

A Palladium Membrane Reactor (PMR) is under consideration for the tritium plant for the International Thermonuclear Experimental Reactor (ITER). The ITER reactor exhaust will contain tritiated impurities such as water and methane. Tritium will need to be recovered from these impurities for environmental and economic reasons. For this purpose a promising device called a palladium membrane reactor (PMR) has been proposed. The PMR is a combined permeator and catalytic reactor. Shift catalysts are used to foster reactions such as water-gas shift, $H_2O + CO \rightarrow H_2 + CO_2$, and methane steam reforming, $CH_4 + H_2O \rightarrow 3H_2 + CO$. Due to thermodynamic limitations these reactions only proceed to partial completion. Thus, a Pd/Ag membrane, which is exclusively permeable to hydrogen isotopes, is incorporated into the reactor. By maintaining a vacuum on the permeate side of the membrane, product hydrogen isotopes are removed, enabling the reactions to proceed to completion.

Others have used membrane reactors to reform methane to conversions beyond equilibrium to demonstrate this technology for industrial applications. Uemiya et al. (1991) used a Pd membrane on Vycor glass with Ni catalyst. Tsotsis et al. (1993) used a commercially available microporous alumina membrane with Ni catalyst. Finally, Shu et al. (1994) used a Pd/Ag membrane with Ni catalyst, which is the most similar to the reactor in this study. Although these reactors produced conversions greater than the equilibrium limit, they did not remove essentially all of the hydrogen as will be required in fusion fuel processing. Good conversions in an industrial application would be 50-90%, while we are interested in achieving 99.99% conversion.

A model has been developed to study the complex interactions in a PMR so that the optimal design can be determined. The model accounts for the coupled effects of transport-limited permeation of hydrogen isotopes and chemical reactions. The permeation model is an extension of previous models that include the effects of temperature, wall thickness, reaction-side pressure, and permeate-side pressure. Reaction rates for methane steam reforming and the water-gas shift reaction are incorporated into the model along with the respective reverse reactions.

The reverse reactions become important as equilibrium is approached. The injected gas mixture is initially far from equilibrium and only the forward reactions are important. As hydrogen is removed from the reacting stream, equilibrium shifts in favor of further impurities conversion. Nevertheless, the methane and water concentrations eventually approach the equilibrium values and the reverse reactions become important.

The model is compared to PMR data and used to investigate the concentration and pressure profiles in the reactor. Due to the interactions of permeation and reaction complex profiles can be produced in a PMR. For example, the water concentration often increases after the inlet to the PMR, forms a maximum value, and then decreases to the low values expected with a PMR. Detailed information like this is required for the design and optimization of PMRs for the ITER tritium plant.

EXPERIMENT DESCRIPTION

Willms et al. (these proceedings) gives a detailed description of the experiments and experimental results, therefore, only a synopsis will be given here. Experiments were conducted with an inlet mixture that the ITER Tritium Plant team is considering as the design mixture for the exhaust of the ITER reactor. The Pd/Ag tube in the PMR was 52 cm in length and had an OD of 0.50 cm. This tube was place inside a 0.87 in. ID tube and the annulus was filled with Ni/Al_2O_3 catalyst. Feed was injected into one end of the annulus and retentate flowed out the other end. Permeate was removed from the inside of the Pd/Ag tube with a vacuum pumping system. Table 1 shows the inlet and outlet conditions for the two experiments analyzed with the PMR model in this paper. Test 1 was the initial tritium experiment and, for safety reasons, only 2.2 % of the hydrogen isotopes were tritium and the balance was hydrogen. In Test 2, 43.3 % of the hydrogen isotopes were tritium and the balance was hydrogen.

Table 1. Experimental conditions and results from Willms et al.

Parameter	Test 1	Test 3
T (°C)	505	574
P (torr)	906	916
Input		
Inert Feed (sccm)	22.0	12.8
CH_4 Feed (sccm)	20.0	13.1
HTO Feed (sccm)	25.2	17.0
HT Feed (sccm)	5.2	3.0
Output		
Inert (mole %)	61.5	61.2
CH_4 (mole %)	0.195	0.210
HTO (mole %)	0.310	0.058
HT (mole %)	0.133	0.110
CO (mole %)	2.45	2.98
CO_2 (mole %)	35.7	34.9
Retentate Flow (sccm)	34.2	21.9
Permeate Pressure (torr)	0.4	0.5
Permeate Flow (sccm)	69.4	48.0
DF	250	360

MODEL DESCRIPTION

A model was developed to investigate the performance of PMRs operating at ITER fuel cleanup conditions. Xu and Froment (1989) have studied the methane steam reforming process extensively and have determined three dominant reactions:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \tag{1}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{2}$$

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \tag{3}$$

They determined intrinsic rates for these reactions in the form of Langmuir-Hinshelwood kinetics:

$$R_1 = \frac{k_1}{P_{H_2}^{2.5} Den^2}\left(P_{CH_4} P_{H_2O} - \frac{P_{H_2}^3 P_{CO}}{K_1}\right) \tag{4}$$

$$R_2 = \frac{k_2}{P_{H_2} Den^2}\left(P_{CO}\, P_{H_2O} - \frac{P_{H_2} P_{CO_2}}{K_2}\right) \tag{5}$$

$$R_3 = \frac{k_3}{P_{H_2}^{3.5} Den^2}\left(P_{CH_4} P_{H_2O}^2 - \frac{P_{H_2}^4 P_{CO_2}}{K_3}\right) \tag{6}$$

where

$$Den = 1 + K_{CO}P_{CO} + K_{H_2}P_{H_2} + K_{CH_4}P_{CH_4} + K_{H_2O}P_{H_2O} \,/\, P_{H_2}$$

and the preexponential factors and activation energies for the reaction rate constants (k_i) and adsorption constants (K_i) are shown in Table 1. K_1, K_2, and K_3 are the equilibrium constants for eqns. 1-3. The model assumes that the flow is one dimensional, steady-state and isothermal[1]. Continuity equations for the retentate are:

$$dF_{CO} = W_{cat}(R_1 - R_2)dz \tag{7}$$

$$dF_{H_2,ret} = \left[W_{cat}\left(3R_1 + R_2 + 4R_3\right) - R_{perm}\right]dz \tag{8}$$

$$dF_{CH_4} = -W_{cat}\left(R_1 + R_3\right)dz \tag{9}$$

$$dF_{CO_2} = W_{cat}(R_2 + R_3)dz \tag{10}$$

$$dF_{H_2O} = -W_{cat}(R_1 + R_2 + 2R_3)dz \tag{11}$$

In the above model, H represents both hydrogen and tritium. The permeation model accounts for the different rates of the two hydrogen isotopes(Ackerman and Koskinas, 1972):

$$dF_{H_2,perm} = R_{perm}\left(\sqrt{P_{H_2,ret}} - \sqrt{P_{H_2,perm}}\right)dz \tag{12}$$

where R_{perm} is a weighted average of the pure hydrogen permeation factor

$$R_{perm,H_2} = \frac{2\pi A_{H_2}}{\ln\left(\frac{r_{in}}{r_{out}}\right)}\exp\left(\frac{-E_{H_2}}{T}\right) \tag{13}$$

and the pure tritium permeation factor

$$R_{perm,T_2} = \frac{2\pi A_{T_2}}{\ln\left(\frac{r_{in}}{r_{out}}\right)}\exp\left(\frac{-E_{T_2}}{T}\right) \tag{14}$$

The Arrhenius parameters for hydrogen and tritium permeation are (Yoshida et al., 1981):

$$A_{H_2} = 1.23x10^{-7}\left(\frac{mol}{cm - s - atm^{0.5}}\right) \tag{15}$$

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[1] Pressure drop is calculated with the Ergun equation in the computer code but this is not presented here since the data analyzed in this paper are essentially isobaric

$$E_{H_2} = 689K^{-1} \tag{16}$$

$$A_{T_2} = 6.34x10^{-8}\left(\frac{mol}{cm - s - atm^{0.5}}\right) \tag{17}$$

$$E_{T_2} = 740K^{-1} \tag{18}$$

Film theory was used to calculate the effect of diffusion on the permeation rate

$$R_{perm} = \frac{2\pi r k_m}{RT}\left(P_{H_{2,wall}} - P_{H_{2,perm}}\right) \tag{19}$$

where r is the outer radius of the membrane tube and the mass transfer coefficient is calculated from the Sherwood number correlation (Rautenbach and Albrecht, 1989).

$$Sh = k_m D\left(3.66^3 + 1.61^3 \operatorname{Re} Sc \frac{D}{L}\right)^{1/3} / D_{H_2-mix} \tag{20}$$

Physical properties were calculated locally with the Chemkin Thermodynamic Data Base code for determining properties of gas mixtures (Kee et al., 1990). The diameter used in the Re calculation is the particle diameter

$$D_p = \sqrt{2r_p L_p + 2r_p^2} \tag{21}$$

based on the length and radius of the catalyst pellets. The diameter used in the Sh calculation is the diameter of the retentate tube, which assumes that hydrogen diffusion within the retentate annulus is not effected by the presence of the catalyst.

The above equations were solved with a fourth order Runge-Kutta method.

Table 1. Arrhenius parameters for the reaction rate expressions.

Rate or Adsorption constant	A_i	E_i/R (K^{-1})
1	$1.17x10^{12}$ (mol-atm$^{1/2}$/g-s)	28900
2	$5.50x10^{2}$ (mol/g-s-atm)	8070
3	$2.82x10^{11}$ (mol-atm$^{1/2}$/g-s)	29300
CO	$8.34x10^{-5}$ (atm^{-1})	-8500
H_2	$6.20x10^{-9}$ (atm^{-1})	-9970
H_2O	$1.77x10^{5}$	10700
CH_4	$6.74x10^{-4}$ (atm^{-1})	-4600

Equilibrium between the reactions in eqns. 1-3 is accounted for in the reaction rate model (eqns. 4-6). However, initial calculations showed that the model and data did not agree using this estimate of the equilibrium. Therefore, equilibrium was calculated for our data using the computer code Solgas (Besmann, 1989). Solgas calculations indicated that carbon was depositing as coke in our reactor and this significantly effected the gas phase equilibrium. These calculations were in good agreement with the PMR data. Therefore, coking was accounted for by incorporating Solgas results into the PMR model. Figure 1 shows Solgas calculations based on the inlet conditions for Test 1. This relationship can be incorporated into the PMR model without introducing significant error because our data are isothermal and isobaric. The carbon balance was adjusted according to Figure 1 via the methane decomposition reaction:

$$CH_4 \leftrightarrow C(s) + 2H_2 \tag{19}$$

This method of estimating coke formation assumes that the methane decomposition reaction moves to equilibrium instantaneously. Intrinsic reaction rates for methane decomposition are not available because in industrial steam reforming applications water partial pressures are kept high to avoid coking.

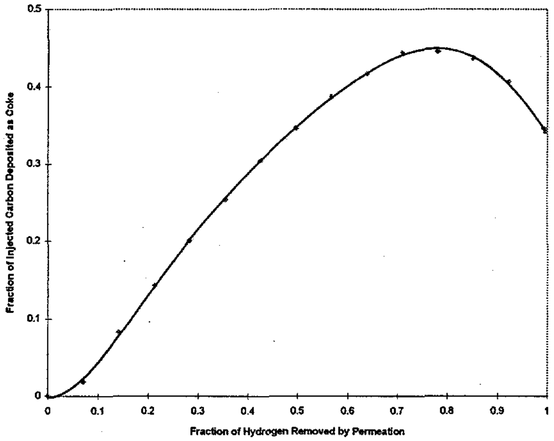

Figure 1. Equilibrium carbon deposition as a function of hydrogen removal for Test 1 (calculated with Solgas).

MODEL RESULTS

Table 2 shows the outlet composition for the data compared to the PMR rate model and the Solgas equilibrium model for Test 1. The rate and equilibrium models agree well, confirming that the hybrid equilibrium model (combination of reaction rates from Xu and Froment (1989) and Solgas) in the PMR model is appropriate. It is evident that the methane decomposition reaction is in equilibrium from the comparison of the experimental and predicted quantity of deposited carbon. Also, the data are within 20% of equilibrium for the water-gas shift reaction (eqn. 2). However, the methane reforming reaction (eqn. 1) is far from equilibrium.

Table 2. Outlet composition (mole %) from data and calculated from the PMR rate model and the Solgas equilibrium model for Test 1 (504 C, 906 torr, outlet decontamination factor=250).

	CO	CO_2	H_2	Inert (He&Ar)	H_2O	CH_4	% Carbon deposited
Data	**2.45**	**35.7**	**0.133**	**61.5**	**.31**	**.195**	**34.4**
PMR Rate Model	**3.18**	**33.7**	**0.259**	**62.3**	**0.573**	**$1.18x10^{-3}$**	**34.3**
Solgas Equilibrium Model	**3.57**	**33.6**	**0.274**	**62.1**	**0.517**	**$1.92\ x10^{-3}$**	**34.3**

Figure 2 shows the decontamination factor (inlet tritium flow rate divided by the outlet tritium flow rate) for Test 1. The model shows that equilibrium should be achieved at a decontamination factor of 1125 within about 22 cm of the entrance to the reactor. Test 1 resulted in a decontamination factor of only 250 with an experimental reactor length of 52 cm. The model predicts a decontamination factor of 250 within 19 cm. Analyses of Tests 2 and 3 also indicate that the reactor was not performing as well as the model predicts. Several possible explanations for the discrepancy exist. First, reaction rates could be in error. The reaction rates of Xu and Froment (1989) were modified for this model, but more importantly, those rates were determined from data at industrial operating conditions which are at much higher H_2O concentrations (to prevent coking) and much higher H_2 concentrations (H_2 is not removed with permeators in industrial applications). Second, experimental error could cause the discrepancy. As mentioned in Willms et al., some problems were encountered measuring the temperature in the reactor during the experiments. It is plausible that the tests were run at a temperatures somewhat below the reported values. This explanation is weakened by the above discussion that indicates the data are in equilibrium (with the exception of the stable methane molecule) at the reported experiment temperature. Finally, it is possible that our catalyst was either deactivated or poisoned during shakedown experiments. This explanation is consistent with the observation that the exit conditions are in equilibrium.

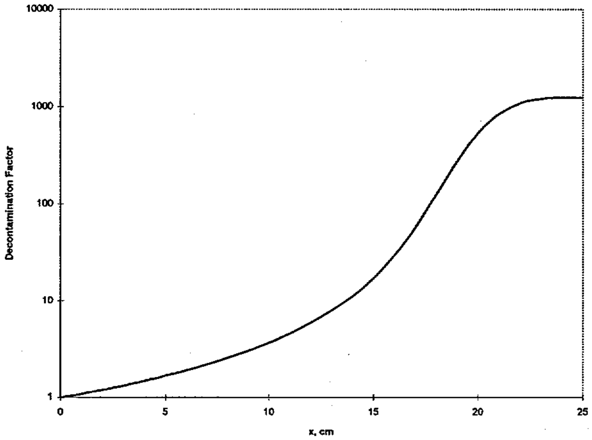

Figure 2. Model results for the decontamination factor for Test 1.

Figure 3 shows the calculated flow profiles of carbon-containing species in the reactor for Test 1. In this plot, F_C is the fraction of the injected carbon that has been deposited as coke. Figure 4 shows the flow profiles of hydrogen-containing species. Figure 5 shows the composition profiles for methane and water. The model predicts that, close to the entrance of the reactor, water reacts slowly and is actually concentrated due to the high permeation rate. Methane reacts more quickly near the entrance due primarily to methane decomposition. Finally, Figure 6 shows the hydrogen gradient between the bulk gas and the gas next to the membrane. It can be seen that the diffusion limitation caused by the hydrogen flux through the membrane is significant but not dramatic.

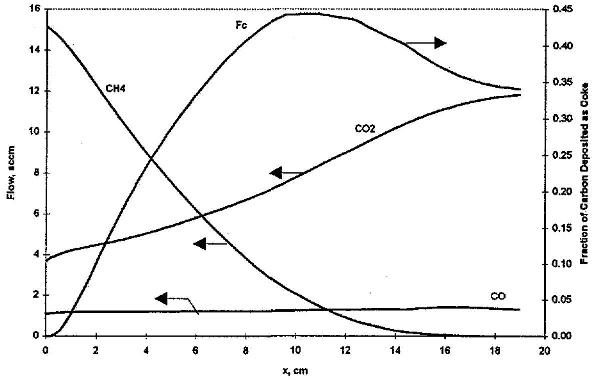

Figure 3. Model predictions of carbon-containing species for Test 1.

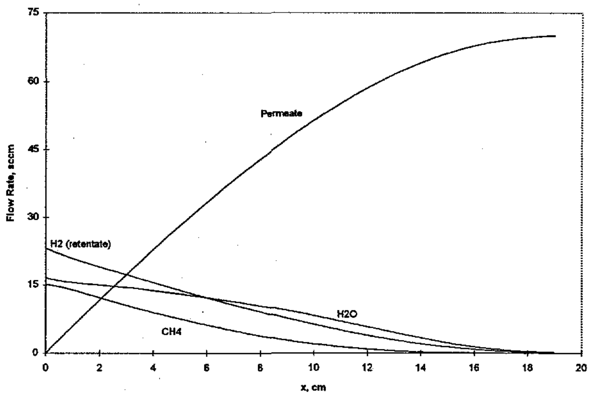

Figure 4. Model predictions of hydrogen-containing species for Test 1.

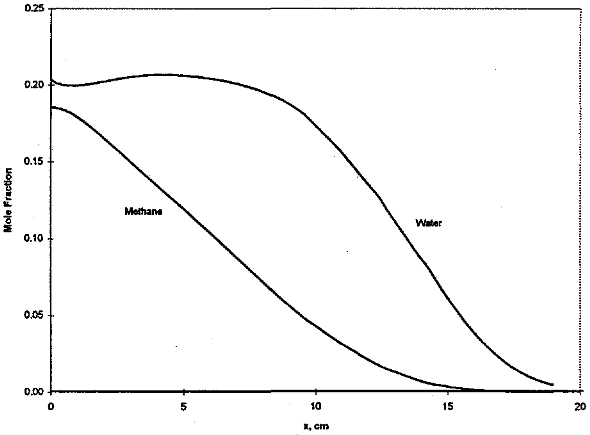

Figure 5. Model predictions of methane and water fractions for Test 1.

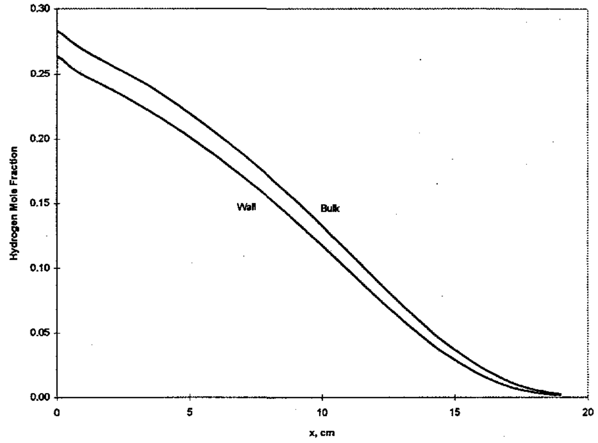

Figure 6. Model predictions for hydrogen gradient across a thin film at the membrane surface for Test 1.

Table 3 shows the results of Test 3, which resulted in a decontamination factor of 360 at a temperature of 572 C. The table shows two PMR model results. The first result does not allow carbon to be transferred from solid coke into the gas phase. The second result allows carbon uptake to occur. Comparison of F_C in Figure 7 to that in Figure 3 demonstrates the difference between these 2 cases. The case with no carbon uptake allowed fits the data of Test 3 much better than the case in which carbon uptake is allowed. Therefore, it is concluded that no coke was available for uptake in the latter part of the reactor during Test 3. Furthermore, the data of Test 2 underwent a transient that was not quite over when the limited tritium supply for injection into the reactor was depleted. It is postulated that coke from previous shakedown experiments was available in excess for uptake during Test 1. During Test 2 the coke in the uptake region was no longer available in excess, resulting in a transient that could not be simulated by our model. Finally, during Test 3, no coke was available in the uptake region. Decontamination factors are high regardless of whether or not carbon is available for uptake.

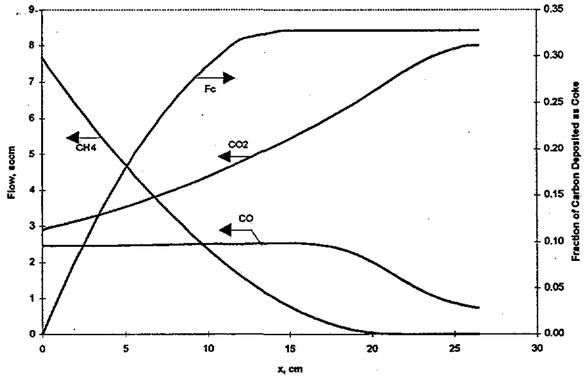

Figure 7. Model prediction of carbon-containing species for Test 3. CH_4, CO_2, and CO profiles are calculated using the solid F_C line.

Table 3. Outlet composition (mole %) from data and calculated from the PMR rate model and the Solgas equilibrium model for Test 3 (572 C, 915 torr, and outlet decontamination factor=360)

	CO	CO_2	H_2	Inert (He&Ar)	H_2O	CH_4	% Carbon deposited
Data	**2.98**	**34.9**	**0.11**	**61.2**	**0.058**	**0.21**	**36.3**
PMR Rate Model, no carbon uptake[1]	**3.60**	**36.9**	**0.141**	**58.9**	**0.481**	**$1.66x10^{-5}$**	**32.4**
PMR Rate Model	**12.7**	**30.7**	**0.330**	**56.0**	**0.266**	**$1.36x10^{-3}$**	**27.0**
Solgas Equilibrium Model	**10.2**	**32.4**	**0.301**	**56.7**	**0.300**	**$7.74x10^{-4}$**	**26.5**

1-No carbon allowed to be converted from coke to gas phase

Table 4 shows the PMR rate model and the Solgas equilibrium model results when the models were constrained to not allow carbon formation. There is a dramatic difference between the predicted and measured outlet concentrations when carbon deposition is not accounted for. These errors were eliminated when the mechanism for carbon deposition (eqn. 19) was incorporated into the code.

Table 4. Same as Table 3, except PMR rate model and Solgas equilibrium model do not allow carbon deposition.

	CO	CO_2	H_2	Inert (He&Ar)	H_2O	CH_4	% Carbon deposited
Data	**2.98**	**34.9**	**0.11**	**61.2**	**0.058**	**0.21**	**36.3**
PMR Rate Model (no graphite)	**35.2**	**15.0**	**0.404**	**49.2**	**0.0574**	**0.0324**	-
Solgas Equilibrium Model (no graphite)	**35.4**	**15.0**	**$3.99x10^{-6}$**	**49.2**	**$5.35x10^{-6}$**	**$3.50x10^{-6}$**	-

CONCLUSIONS

A PMR model has been developed and compared to tritium-containing experiments relevant to ITER. The model uses intrinsic kinetics for methane steam reforming. The kinetics are adapted to ITER conditions by adding carbon deposition via the methane decomposition reaction. Model results indicate that much higher decontamination factors should be achievable than the already high values measured in our experiments. The model shows that it is possible for regions of coking and decoking to exist within a PMR. These effects do not result in lower decontamination factors.

This model has led to a better understanding of PMRs operating at ITER conditions and will be instrumental in the design and operation of future PMR experiments. Benchmarking of the model to PMR data elucidated the need to incorporate a coking mechanism into the model. It is intended that this model will be developed into a robust model that includes coking reaction rates and fully-coupled gas-coke equilibrium.

NOMENCLATURE

A	Preexponential Factor
D	Diameter (cm)
$D_{H2\text{-}mix}$	Diffusivity of H_2 in the local gas mixture (cm^2/s)
DF	Decontamination Factor, inlet tritium flow rate divided by the outlet tritium flow rate

E	Activation Energy (K^{-1})
F_i	Molar Rate (mol/s)
k_i	Reaction Rate Constant (see Table 1 for units)
k_m	Mass Transfer Coefficient (cm/s)
K_i	Adsorption Constant (see Table 1 for units)
L	Length (cm)
P	Pressure (atm)
r	Radius (cm)
R_i	Reaction Rate (mol/g-s) or Permeation Rate (mol/cm-s)
R	Universal Gas Constant
T	Temperature (K)
Sh	Sherwood Number
W_{cat}	Linear density of catalyst (g/cm)
z	Axial Length of Reactor (cm)

SUBSCRIPTS

p	Catalyst pellet
perm	Permeation
ret	Retentate
wall	At the membrane wall

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