RESUMEN

En la presente Tesis se analiza el comportamiento de un reactor de membrana en el que se lleva a cabo la reacción de desplazamiento de gas de agua (WGS) sobre un catalizador comercial de Fe/Cr con el objetivo de purificar una corriente de gas de síntesis para alimentarla finalmente a una celda de combustible tipo PEM.

Se simula la operación de un reactor multitubular de membrana inerte. En él, se extrae el H_2 selectivamente por medio de membranas tubulares de Pd/Ag soportadas α-Al_2O_3 permitiendo el desplazamiento del equilibrio. El catalizador se encuentra ubicado en los tubos y por la carcasa circula un gas de arrastre. Se evalúa la importancia de considerar los efectos térmicos que tienen lugar en este reactor, en particular, cuando se trabaja a escalas mayores que las que generalmente se consideran en el laboratorio. Por medio de un modelo matemático 1D pseudohomogéneo se estudia la influencia de algunas variables operativas y de diseño sobre los perfiles de temperatura, la conversión y la recuperación de hidrógeno. Se demuestran las ventajas de utilizar un reactor de membrana frente a un reactor convencional y se comparan las operaciones en las que la corriente de reactivos y permeado circulan en modo cocorriente por un lado, y cuando circulan en modo cotracorriente por otro. Debido a la retroalimentación de calor que existe cuando se opera en modo contracorriente, se analiza la estabilidad del reactor bajo las condiciones estudiadas. Se extiende luego el análisis a un diseño en el que se modifica la ubicación de catalizador. Con el propósito de aumentar la recuperación, se analizan diferentes estrategias para aumentar la fuerza impulsora para la permeación tales como incrementar la presión operativa, el caudal de gas de arrastre y el area de permeación. Además, se presentan expresiones algebraicas que permiten estimar el máximo incremento de temperatura que podría tener lugar en un reactor de membrana. Por otro lado, se incluye el procedimiento de cálculo de la conversión y recuperación de equilibrio en un reactor de membrana operando a cocorriente. Por último, se ajustan resultados experimentales obtenidos en el Instituto de Investigaciones en Catálisis y Petroquímica (INCAPE). Los catalizadores considerados, en este caso, son más activos que el catalizador commercial de Fe/Cr comúnmente utilizado para llevar a cabo la reacción de WGS a altas temperaturas. Por tal motivo, se plantea un modelo unidimensional heterogéneo con el fin de cuantificar la presencia de fenómenos difusionales externos.

ABSTRACT

The present Thesis analyses the reaction behavior of a membrane reactor where the water-gas shift (WGS) reaction is conducted over a Fe/Cr commercial catalyst. The aim of the investigated system is the purification of a synthesis gas stream for PEM fuel cell feeding.

The operation of a multitubular reactor with inert membranes is simulated. The use of Pd/Ag tubular composite membranes permits the selective extraction of hydrogen leading to a shift in the chemical equilibrium of the WGS reaction. In this work, the relevance of considering the thermal effects occurring in the reactor is evaluated, in particular, in the situations where the scale of the system is higher than the one usually handled in lab works. A 1D pseudohomogeneous mathematical model is profited here to study the influence of operating and design variables over axial profiles of temperature, conversion and hydrogen recovery.

The advantages in the selection of a membrane reactor design over a conventional reactor for performing the WGS reaction are reported. A performance comparison for the reactor operating with permeate and retentate streams circulating in the same (cocurrent) or opposite (countercurrent) directions is presented as well. Due to the heat feedback phenomenon verified when countercurrent operation is selected, the stability in the reactor operation is analyzed. Moreover, algebraic equations to estimate the maximum possible temperature rise in the membrane reactor are reported here.

For the case of a membrane reactor under cocurrent regime, the calculation procedure for both conversion and equilibrium recovery is presented. With the aim of improving the hydrogen recovery, different strategies including increasing the operation pressure or using diverse sweep gases are analyzed towards an enhancement of the permeation driving force.

A fitting work of experimental results measured at Instituto de Investigaciones en Catálisis y Petroquímica (INCAPE) is also reported in this Thesis. The two different catalysts used in the experiments present higher activities than the Fe/Cr commercial catalyst usually selected for high temperature WGS. Therefore, a 1-D heterogeneous mathematical model is solved to quantify the impact of external diffusion phenomena. The math model allows a satisfactory reproduction of the experimental results for the two catalysts evaluated.

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