Determining factors involved in the preliminary design of a non isothermal membrane reactor

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Introduction

The growing demand of energy in many industrial fields requires the conceiving of more efficient production and utilization systems in a logic of sustainable development. Hydrogen results one of the more attractive energy carrier for its versatility ranging from stationary and mobile applications, as clean fuel, to the use in different refinery processes. In the last years, significant efforts have been addressed towards new technologies, alternative to the conventional ones and economically viable, to obtain hydrogen at a high purity level.

Palladium-based membrane reactors, combining the separation and reaction steps in a single unit, can be successfully used for the selective removal of the hydrogen produced in a chemical reaction.

In this work, by means of a theoretical analysis of concentration and temperature profiles for the water gas shift reaction, it has been possible to select opportunely both sweep gas flow rate and temperature, reactor size, catalyst distribution in order to enhance CO conversion and control the intensity of temperature hot spots.

Theoretical approach

Radial and axial concentration and temperature profiles, obtained by means of a two–dimensional pseudo-homogeneous model, have been used to describe the behavior of a non isothermal tubular packed membrane reactor (tube and shell configuration) as a function of different operating conditions (e.g. temperature, pressure, feed molar ratio, sweep gas flow rate) and design parameters (reactor length and diameter). The model takes into account the convective term in the axial direction and the diffusive contribution in the radial direction, while it neglects the axial dispersion for both heat and mass transport, according to the criterion concerning minimum ratio between reactor length and particle diameter [Froment and Bischoff, 1990]. In order to describe the heat transfer in radial direction from the reactor core to the wall, a heat transfer coefficient *whtc* has been introduced in combination with to the effective radial thermal conductivity *ertC*. Both coefficients depend on fluidynamics (Re) and ratio between particle and reactor diameters. Hydrogen permeation rate values, obtained experimentally in the temperature range of interest for this study [Basile *et al.*, 2001], and Temkin's kinetic expression for WGSR [Newsome and Kellog, 1980] have been utilized. A more detailed description of all assumption of the model has been given elsewhere [Chiappetta *et al.*, 2006].

Results and discussion

When the inherent heat of reaction is significant and the heat exchange across the membrane is limited, a temperature increase occurs until the exchanged heat amount overcomes the one produced in the reaction. It determines the appearance of a maximum in the temperature profile along the axial direction, whose value is a strong function of the radial position, see figure 1.
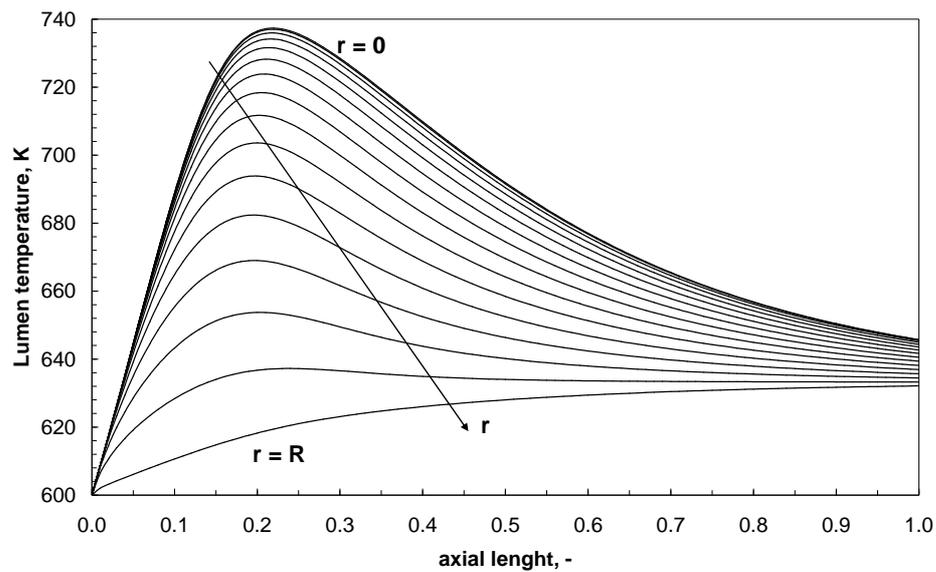
Figure 1. Temperature profile along the reactor at a feed pressure equal to 500 kPa and inlet feed temperature of 600 K for different radial positions.

As shown in figure 2, the increase of the feed pressure (p) produces a high and quick conversion of the reagents that becomes more important over 500 kPa as indicated by increasing slope of the curves. The fast generation of the products, producing a significant heat amount, favors the endothermic reverse reaction with respect to the exothermic one. Therefore, it opposes to the advantageous shifting of the equilibrium promoted by the slow hydrogen permeation. As a consequence, if the conversion increases gradually in the whole catalytic bed at 110 kPa, it remains almost constant at pressure values higher than 500 kPa for an adimensional length > 0.2.
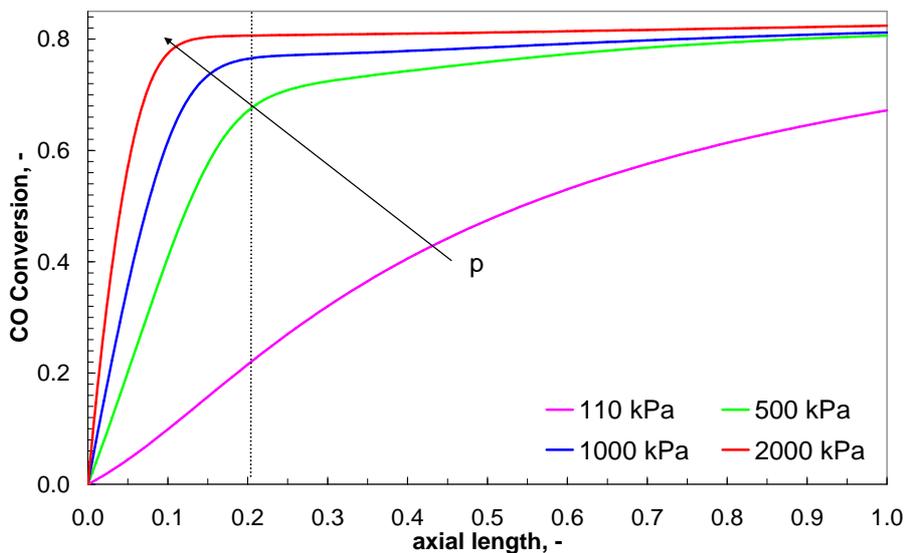
Figure 2. CO conversion *vs.* adimensional axial length at different feed pressure for L/D = 2.

The presence of the sweep gas in membrane reactors is important since it enhances the hydrogen permeating flow by improving the driving force across the membrane. In non-isothermal membrane systems where exothermic reactions occur, sweep gas favors also the heat exchange allowing a better temperature control without a significant loss in the hydrogen permeation. Therefore, the choice of the sweep gas flow rate ten times higher than the feed gas flow rate and a temperature equal to the feed temperature in the lumen side (600 K) has a beneficial effect on both the driving force for hydrogen permeation and temperature profile since it avoids the risk of dangerous runaways without a relevant conversion loss.

For what concerns the membrane reactor size, at the same membrane surface, it is possible to observe in figure 3 that a short unit ($\frac{L}{D} = 2$) allows a high conversion value (84.2%) but also the most dangerous hot spot ($T_{max} = 980$ K at 110 kPa) as a consequence of the high heat of reaction only partially balanced by a limited heat transfer towards the shell side (considerable resistance in radial direction). At the same pressure value, a reactor with $\frac{L}{D} = 120$ is characterized by a low conversion value and a progressive increase of the lumen temperature, without the presence of a hot spot. This is due to the more effective cooling action of the sweep gas that, by reducing the temperature, slows down the reaction and the permeation rates.
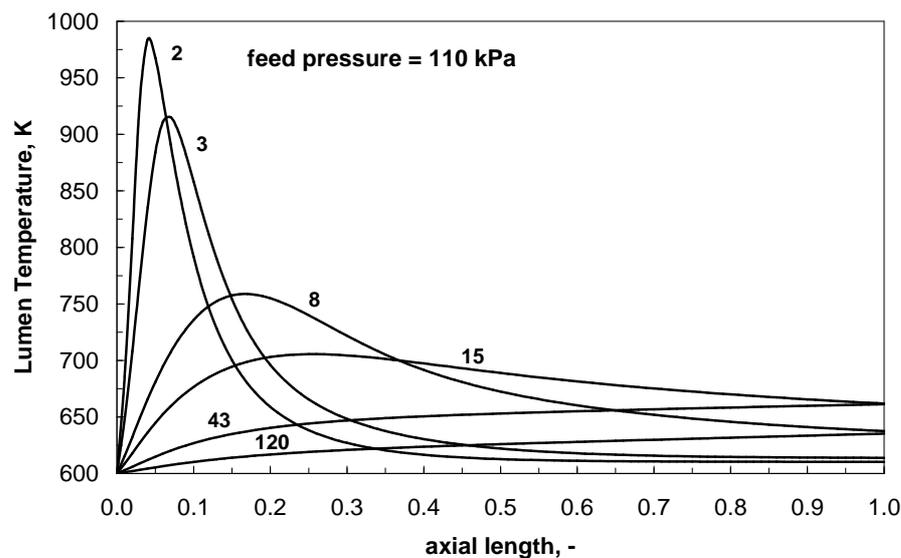
Figure 3. Axial temperature profile on lumen side for some representative membrane reactors at different L/D ratios.

Another mode to control the intensity of temperature hot spot is to operate on the catalyst distribution. As previous discussed, next to the membrane reactor entry an excess of heat is generated by the fresh reagents. Therefore, it has been considered the opportunity to dose the catalyst along the membrane reactor. The simulations, in Figure 4, show how a catalyst mass that increases linearly along the membrane reactor produces a temperature hot spot less significant with respect to an exponential distribution. The latter mode, however, results still more advantageous than a constant allotment of the catalyst. CO conversion is not

markedly affected by the different distributions since the substantial difference occurs close to the reactor entry.
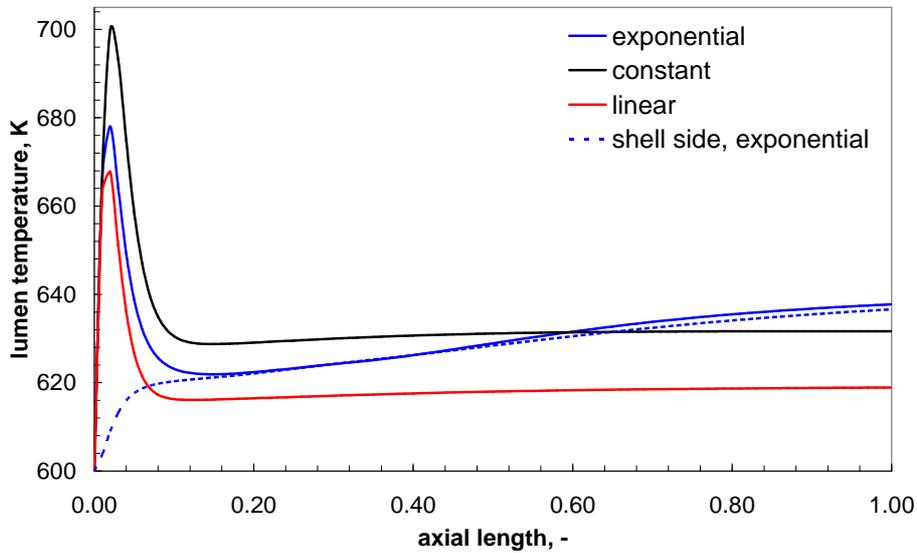
Figure 4. Lumen temperature vs. axial length for three different catalyst distributions along the membrane reactor at a feed pressure of 500 kPa.

Referring to two parameters widely used for describing the heat transfer in packed-bed reactors, figure 5 shows how *ertC* affects the temperature hot spot in a more significant way than *whtc*. For this reason, it is recommendable to operate on *ertC* rather than on *whtc* in order to improve the efficiency of the heat exchange. Only in presence of high *ertC* values, changes in *whtc* produce remarkable effects on temperature profiles.
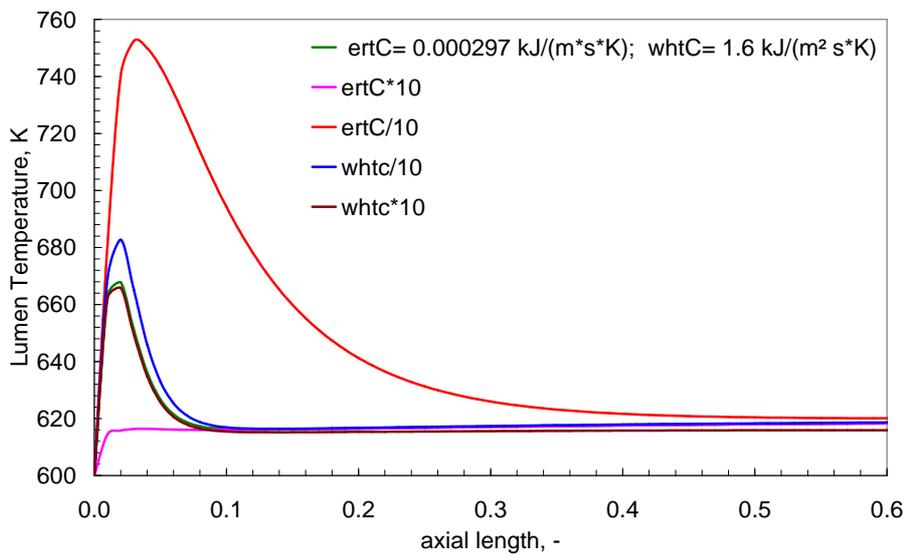
Figure 5. Lumen temperature vs. axial length at different *ertC* and *whtc* values at a feed pressure of 500 kPa.

Conclusions

At all investigated operation conditions on the reactor axis the highest deviations with respect to the inlet feed temperature are observed.

The use of a sweep gas, although causes a dilution of hydrogen in permeate stream, is a useful mode to control temperature hot spots along the membrane reactor without a significant conversion loss, but its effect is more marked when the heat exchanged is effective.

At fixed membrane surface, a short reactor is characterized by a high conversion value combined to relevant hot spots close to the feed gas entry; on the other hand a reduced reagent conversion is achieved in a longer reactor.

A linear distribution of the catalyst mass allows to reduce the hot spot in the reactor without changing the CO conversion.

When a better heat exchange is realized (high *ertC* and *whtc* values), the temperature hot spot is reduced preserving the CO conversion and hydrogen permeation.

References

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