Numerical Evaluation of a Membrane-Assisted Fluidized Bed Reactor for Use in Chemical Switching Reforming

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Abstract – Chemical Switching Reforming (CSR) is a promising new reactor concept for pure hydrogen production with integrated CO₂ capture. Ideal operation of a CSR reactor can convert feed streams of air and fuel/steam to high-purity streams of H₂, CO₂ and N₂. This is achieved through the insertion of hydrogen perm-selective membranes into the reactor to extract pure H₂ and shift the steam reforming and water-gas shift reactions equilibria towards complete conversion. This study reports a first simulation study of the performance of a full CSR cycle.

The membranes form an integral part of the CSR process and closure laws related to the membrane permeability has a great influence on the process performance. However, membrane performances reported in the literature vary over more than an order of magnitude, thereby introducing a degree of uncertainty in this critical model parameter. A study of the effect of different membrane permeabilities was therefore completed to reveal that larger permeabilities allow for greater fuel throughput rates for a given reactor size and membrane surface area, but also activate additional mass transfer limitations stemming from the radial volume fraction segregation in the bed.

The full CSR cycle simulation demonstrated complete O₂ conversion in the air stage and a gradual increase in H₂ and CO formation in the fuel stage. The gradually changing reactor performance in the fuel stage was primarily a result of the oxygen carrier material getting gradually more reduced as the cycle progresses, thereby reducing the rates of complete combustion of H₂ and CO to H₂O and CO₂. Despite a small amount of undesired mixing between CO₂ and N₂ right after the switch from fuel to air and vice versa, a high degree of CO₂ separation was achieved together with good levels of hydrogen recovery.

Nomenclature

1.1 Main Symbol definitions

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>Volume fraction</td>
</tr>
<tr>
<td>φ</td>
<td>Kinetic energy transfer rate (kg/m.s³)</td>
</tr>
<tr>
<td>γ</td>
<td>Dissipation rate (kg/m.s³)</td>
</tr>
<tr>
<td>Θ₀</td>
<td>Granular temperature (m²/s²)</td>
</tr>
</tbody>
</table>
\( \rho \) Density (kg/m\(^2\))
\( \bar{\tau} \) Stress tensor (kg/m.s\(^2\))
\( \tau_w \) Particle shear force at the wall (N)
\( \bar{v} \) Velocity vector (m/s)
\( \nabla \) Del operator / Gradient (1/m)
\( a_0 \) Initial specific surface area of reactant in the oxygen carrier (m\(^2\)/kg)
\( C \) Molar concentration (mol/m\(^3\))
\( E_a \) Activation energy (kJ/mol)
\( \bar{g} \) Gravity vector (m/s\(^2\))
\( h \) Enthalpy (J/kg)
\( I \) Identity tensor
\( \bar{J} \) Diffusive flux ((kg/(m\(^2\).s))
\( J_{\text{H}_2} \) Diffusive flux ((kg/(m\(^2\).s))
\( K_{sg} \) Momentum exchange coefficient (kg/(m\(^3\).s))
\( k \) Diffusion coefficient (kg/m.s)
\( k_j \) Reaction rate constant (mol\(^{(1-n)/2-3n} \cdot s\))
\( k_i \) Reaction rate constant (mol.bar\(^{0.5} \cdot kg_{Ni}.s\))
\( k_2 \) Reaction rate constant (mol/(bar.kg_{Ni}.s))
\( k_3 \) Reaction rate constant (mol.bar\(^{0.5} \cdot kg_{Ni}.s\))
\( \dot{m} \) Mass flow rate (kg/s)
\( n \) Order of reaction
\( P \) Permeability (mol.s\(^{-1}\).m\(^{-1}\).Pa\(^{-n}\))
\( p \) Pressure (Pa)
\( \bar{q} \) Heat flux (W/m\(^2\))
\( Q \) Flow rate of enthalpy (W)
\( r_j \) Reaction rate (mol/(s.kg_{NiO}))
\( r_1, r_2, r_3 \) Reaction rate (mol/(s.kg_{Ni}))
\( S \) Mass/species source term (kg/(m\(^3\).s))
Introduction

Autothermal Chemical Looping Reforming (CLR) is a promising technology for hydrogen production with integrated CO₂ capture [1]. Similar to Chemical Looping Combustion, CLR is conventionally carried out in two interconnected fluidized bed reactors where an oxygen carrier extracts oxygen from air in one reactor and supplies this oxygen in a nitrogen-free environment for fuel combustion in the fuel reactor. This results in inherent separation of CO₂ and N₂ with a much lower energy penalty than usually associated with other CO₂ capture processes.

In the conventional CLR process, natural gas is transformed into syngas through the steam methane reforming reaction after which it must still be shifted to H₂ and CO₂ and separated in
a subsequent shift reactor and pressure swing adsorption unit if pure $\text{H}_2$ is the desired end
product. However, these three steps can conceivably be integrated into one if hydrogen perm-
selective membranes are introduced into the reactor resulting in a thermodynamically
favourable process [2]. This process modification would extract a stream of pure hydrogen
form the reactor and, in the ideal case of infinite membrane surface area, can result in a pure
$\text{CO}_2$ stream at the reactor outlet. Depending on prevailing market conditions, this pure $\text{CO}_2$
stream together with the pure $\text{N}_2$ stream from the air reactor can potentially result in
additional revenue streams to the plant.

The resulting highly intensified membrane-assisted CLR process can potentially be further
improved by eliminating the complexities of solids circulation between reactors, especially at
higher pressures. High pressure operation would be very important for the membrane assisted-
CLR process in order to 1) increase the driving force across the membrane and thereby reduce
the amount of membrane surface area required for a given fuel throughput and 2) deliver a
high pressure $\text{CO}_2$ stream for efficient compression, transport and storage. In order to allow
for relatively easy pressurization and process scale-up, it is therefore proposed that the CLR
process be carried out in a single reactor where the oxygen carrier/catalyst is alternatively
exposed to fuel and air streams. This concept has recently been experimentally demonstrated
[3] and thermodynamically assessed [4] for CLC application and should be directly
extendable to the CLR process. For this reason, this paper investigates the new process
concept of membrane-assisted Chemical Switching Reforming (CSR).

Due to the early stage of development of this concept, only a preliminary numerical
investigation into the operation of the CSR concept is presented here. Closure models
available in the literature are utilized and recommendations are given for future work.

3 Simulations

3.1 Equation system

The Eulerian multifluid approach was used for the numerical simulations in this study. In this
approach the gas and solids are treated as interpenetrating continua, each with its own set of
transport equations for mass, momentum, species and energy. Mass was conserved for each
phase ($q$) as follows, where the right hand source term accounts for mass transfer due to
heterogeneous reactions:

$$
\frac{\partial}{\partial t} \left( \alpha_q \rho_q \right) + \nabla \cdot \left( \alpha_q \rho_q \vec{v}_q \right) = \alpha_q S_q
$$

Equation 1

Momentum conservation was calculated as follows for the gas and solid phases, respectively:

$$
\frac{\partial}{\partial t} \left( \alpha_g \rho_g \vec{v}_g \right) + \nabla \cdot \left( \alpha_g \rho_g \vec{v}_g \vec{v}_g \right) = -\alpha_g \nabla p + \nabla \cdot \vec{\tau}_g + \alpha_g \rho_g \vec{g} + K_{sg} \left( \vec{v}_s - \vec{v}_g \right) + S_{g}^0
$$

Equation 2

$$
\frac{\partial}{\partial t} \left( \alpha_s \rho_s \vec{v}_s \right) + \nabla \cdot \left( \alpha_s \rho_s \vec{v}_s \vec{v}_s \right) = -\alpha_s \nabla p - \nabla \cdot \vec{\tau}_s + \alpha_s \rho_s \vec{g} + K_{gs} \left( \vec{v}_g - \vec{v}_s \right) + S_{s}^0
$$

Equation 3
The inter-phase momentum exchange coefficient \( K_{gs} = K_{sg} \) was modelled according to the Syamlal and O’Brian drag model [5].

The kinetic theory of granular flows (KTGF) was applied to model the solids phase stresses. In this method the random motion of particles is likened to the thermal motion of molecules in a gas using the concept of granular temperature. The conservation equation for granular temperature is as follows:

\[
\frac{3}{2} \left[ \frac{\partial}{\partial t} (\alpha_s \rho_s \Theta_s) + \nabla \cdot (\alpha_s \rho_s \vec{v}_s \Theta_s) \right] = \left( -p_s \vec{T} + \vec{F} \right) : \nabla \vec{v}_s + \nabla \cdot \left( k_{\Theta_s} \nabla \Theta_s \right) - \gamma_{\Theta_s} + \phi_{gs} \quad \text{Equation 4}
\]

This partial differential equation was simplified to an algebraic equation by neglecting the convection and diffusion terms. This assumption is often used in dense, slow moving fluidized beds, where the local generation and dissipation of granular temperature far outweighs the transport by convection and diffusion [6]. The two final terms on the right hand side are the collisional dissipation of energy [7] and the interphase exchange between the particle fluctuations and the gas phase [8].

Solids stresses are calculated according to shear and bulk [7] viscosities due to particle momentum exchange through translation and collision. The shear viscosity consists of three parts: collisional [5, 8], kinetic [5] and frictional [9].

Granular temperature, as well as the radial distribution function (measure of the average distance between particles), is used to determine the solids pressure \( p_s \) in Equation 3. The solids pressure formulation by Lun et al. [7] was complemented by the radial distribution function of Ogawa and Oshima [10].

Species are also conserved for both the gas and solids phases.

\[
\frac{\partial}{\partial t} (\alpha_q \rho_q \frac{q}{Y_{q.j}}) + \nabla \cdot (\alpha_q \rho_q \vec{v}_q \frac{q}{Y_{q.j}}) = \nabla \cdot \alpha_q \vec{J}_{q,j} + \alpha_q S_{q,j} \quad \text{Equation 5}
\]

Finally, energy was conserved as follows:

\[
\frac{\partial}{\partial t} (\alpha_q \rho_q h_q) + \nabla \cdot (\alpha_q \rho_q \vec{v}_q h_q) = -\alpha_q \frac{\partial h_q}{\partial t} + \vec{F} : \nabla \vec{v}_q + \nabla \cdot \vec{q}_q + S_q^k + Q_{pq} + \left( m_{pq} h_{pq} - \dot{m}_{pq} h_{pq} \right) \quad \text{Equation 6}
\]

Interphase heat exchange (second last term on the right) is modelled according to Gunn [11]. The heat of reaction (third term from the right) and energy transfer due to interphase mass transfer (final term on the right) result from the heterogeneous and catalytic reactions included in this study.

The CSR process incorporates numerous chemical reactions that can be divided into three different groups: the oxidation of the oxygen carrier, the reduction of the oxygen carrier and the catalytic reactions in the reduction stage. The reactions included in the reaction mechanism and the rates used vary considerably in the literature, as described by Zhou [12]. Despite this, all the reactions involved in this process proceeded to equilibrium under the conditions studied, therefore the variation in literature reaction rates become less important for this study. However, it remains an important area for future CSR experimental work.

Four heterogeneous reactions between the gas and the solids were included in this study:
These heterogeneous reactions were modelled using the shrinking core model (SCM), assuming that the rate is limited by the chemical reaction in the grains. The following general form is used for the rate equations of these reactions:

\[ r_j = a_0 k_j C_i^n (1 - X)^{2/3} \]  \hspace{1cm} \text{Equation 7}

In Equation 7, \( C_i \) is the molar concentration of the gas species reacting with the oxygen carrier. For the oxidation reaction \( X \) is the conversion of Ni to NiO and for the reduction reactions it is the conversion of NiO to Ni. The rate constant, \( k_j \), is a function of temperature in a standard Arrhenius equation. The various rate parameters used for the oxygen carrier reactions are summarised in Table 1 [13].

\[
\begin{array}{|c|c|c|c|}
\hline
\text{Gas species} & k_{j,0} \ (\text{mol}^{1-n} \text{m}^{2-n} \text{s}^{-1}) & E_{a,j} \ (\text{kJ/mol}) & n_j \\
\hline
O_2 & 1.8 \times 10^{-3} & 7 & 0.2 \\
CH_4 & 7.1 \times 10^{-1} & 78 & 0.8 \\
H_2 & 9.3 \times 10^{-3} & 26 & 0.5 \\
CO & 5.2 \times 10^{-3} & 25 & 0.8 \\
\hline
\end{array}
\]

Several solid catalysed reactions also occur in the reduction stage, with Ni acting as catalyst. The following combination of reactions are included in the numerical model used in this study [14], namely steam methane reforming (1), water gas shift (2) and overall steam methane reforming (3):

\[ CH_4 + H_2O \leftrightarrow CO + 3H_2 \]
\[ CO + H_2O \leftrightarrow CO_2 + H_2 \]
\[ CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \]

The rates of these reactions are calculated from the set of equations first proposed by Xu & Froment [14]:

\[ r_i = \alpha_{\text{cat}} \frac{k_1}{p_{H_2}^{2.5}} (p_{CH_4} p_{H_2O} - \frac{p_{H_2}^3 p_{CO}}{K_1}) / (DEN)^2 \]  \hspace{1cm} \text{Equation 8}
\[ r_2 = \alpha_{cat} \frac{k_2}{p_{H_2}} \left( \frac{p_{CO}p_{H_2,O}}{p_{H_2}p_{CO_2}} \right) / (DEN)^2 \]  
Equation 9

\[ r_3 = \alpha_{cat} \frac{k_3}{p_{H_2}} \left( \frac{p_{CH_4}p_{H_2,O}^2}{p_{H_2}^4p_{CO_2}} \right) / (DEN)^2 \]  
Equation 10

\[ DEN = 1 + K_{CO}p_{CO} + K_{H_2}p_{H_2} + K_{CH_4}p_{CH_4} + K_{H_2,O}p_{H_2,O} / p_{H_2} \]  
Equation 11

Added to the rate equations of Xu and Froment [14] for this study, \( \alpha_{cat} \) is the catalytic activity of the oxygen carrier and has a value of 1 when the oxygen carrier is completely reduced. This factor is calculated as a function of NiO conversion to nickel through the following equation, where \( a \) and \( b \) have values of 0.19 and 0.81, respectively [15].

\[ \alpha_{cat} = aX + bX^2 \]  
Equation 12

The values of the adsorption coefficients used in this study are obtained from Oliveira [16]. Table 2 summarises the kinetic [16] and equilibrium [12] parameters used in this study.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Kinetic parameters</th>
<th>Equilibrium parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( k_{j,0} ) (mol^{-1} m^{-3} s^{-1})</td>
<td>( E_a ) (kJ / mol)</td>
</tr>
<tr>
<td>Methane reforming</td>
<td>5.83 \times 10^{11}</td>
<td>218.55</td>
</tr>
<tr>
<td>Water gas shift</td>
<td>2.51 \times 10^{14}</td>
<td>73.523</td>
</tr>
<tr>
<td>Overall methane reforming</td>
<td>4.67 \times 10^{13}</td>
<td>236.85</td>
</tr>
</tbody>
</table>

3.2 Geometry and mesh

The CSR process with hydrogen extraction was investigated by using a 2D representation of a fluidized bed containing hydrogen extracting membranes. 2D simulations were selected at this stage to efficiently gain a first impression of process performance. A staggered pattern of tubes was used to extract hydrogen produced in the reactor. Two different sets of geometry and mesh were used in this study, one for investigating the effect of the rate of hydrogen flux through the membranes (Section 4.1) and the other to perform a simulation of the complete cycling system (Section 4.2). These two setups are compared in Table 3.
Table 3: Comparison of geometry and mesh configurations for the two different investigations in this study

<table>
<thead>
<tr>
<th>Property</th>
<th>Membrane investigation</th>
<th>Cyclic study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor height</td>
<td>0.5 m</td>
<td>1 m</td>
</tr>
<tr>
<td>Reactor width</td>
<td>0.1 m</td>
<td>0.29 m</td>
</tr>
<tr>
<td>Membrane diameter</td>
<td>5 mm (circular)</td>
<td>10 mm (square)</td>
</tr>
<tr>
<td>Membrane spacing</td>
<td>15 mm between the centres of all membranes</td>
<td>40 mm spacing between the centres in the x-direction, 40 mm spacing in the y-direction</td>
</tr>
<tr>
<td>Rows of membranes</td>
<td>30 rows</td>
<td>18 rows</td>
</tr>
<tr>
<td>Total number of membranes</td>
<td>195</td>
<td>126</td>
</tr>
<tr>
<td>Mesh</td>
<td>Paved cells varying from 1 mm next to the membranes to 5 mm in the freeboard</td>
<td>10 mm structured cells aligned with the membrane arrangement.</td>
</tr>
</tbody>
</table>

The mesh used in the cycling study was substantially cruder than the one used in the detailed membrane permeability study. This was done in order to achieve sufficient simulation speed to complete several full CSR cycles in order to reach pseudo-steady state operation and report meaningful results.

3.3 Initial and boundary conditions

The solution was initialized with zero velocity and no solids, after which solids were patched in at a volume fraction of 0.3 to the initial static bed height of 0.9 m for the cyclic study. For the membrane permeation study, the bed was initialized with a solids volume fraction of 0.6 up to a height of 0.4 m. Much of these solids were blown out of the domain at the higher fluidization velocities investigated, resulting in an expanded bed height close to the height of the membranes.

The walls were specified with a no-slip boundary condition for the gas phase and a specularity coefficient of 0.5 for the solids. The gas velocity and composition at the inlet boundary was altered between the different numerical setups and between the reduction and oxidation stages in the cyclic process. Details regarding this are given in Table 4 and Table 5 in the Results and Discussion section.

The membrane boundary condition is specified as a sink to remove hydrogen and the associated energy at a specified rate. The rate of hydrogen extraction was determined as follows [17]:

\[
J_{H_2} = \frac{P_{mem}}{t_{mem}} (p_{H_2,\text{fluid}}^n - p_{H_2,\text{perm}}^n)
\]

Equation 13
\[ P_{\text{mem}} = e^{a T^2 + n T + b} \]  
\[ n = b_1 T^2 + b_2 T + b_3 \]

The constant values used are \( a_1 = 5.183 \times 10^{-5} \), \( a_2 = -6.474 \times 10^{-2} \), \( a_3 = -7.235 \), \( b_1 = -3.910 \times 10^{-6} \), \( b_2 = 4.964 \times 10^{-3} \) and \( b_3 = -0.5697 \). A membrane thickness, \( t_{\text{mem}} \), of \( 4.5 \times 10^{-6} m \) was used.

### 3.4 Material properties

Heat capacities for the individual species were calculated as temperature dependent polynomials. The individual species were CH\(_4\), H\(_2\)O, H\(_2\), CO and CO\(_2\) in the gas phase and NiO, Ni and Al\(_2\)O\(_3\) in the solids. The gas density was calculated from the ideal gas law and the viscosity via kinetic theory. Solids densities of 4002 kg/m\(^3\), 5345 kg/m\(^3\) and 2415 kg/m\(^3\) were used for NiO, Ni and Al\(_2\)O\(_3\), respectively. A particle size of 150 µm was used. These densities correspond to an assumed porosity of 0.4 for the solids.

### 3.5 Solver settings

The commercial software package, FLUENT 13.0 was used as the flow solver. The phase coupled SIMPLE scheme [18] was used for pressure-velocity coupling. Spatial discretization of the remaining equations was performed using the higher order QUICK scheme [19]. 1\(^{st}\) order implicit temporal discretization was used, which is sufficient for dense fluidized beds where the flow velocities are relatively low in general.

### 4 Results and discussion

Results will be presented in two parts: 1) a brief investigation into the primary uncertainty involved in the CSR process; membrane permeability, and 2) a numerical demonstration of a full CSR cycle.

#### 4.1 Membrane permeability

The hydrogen flux over the membranes has obviously a highly significant effect on the overall process performance, since it controls the final equilibrium gas composition produced. An increased hydrogen extraction rate will result in less hydrogen bypass in the retentate gas, as well as better CO\(_2\) selectivity. A comparison of the hydrogen flux obtained in various different literature studies [17, 20-25] are shown in Figure 1 for different fluid partial pressures and a permeate partial pressure of 0.05 bar.
As seen above, the diffusive flux achievable across hydrogen perm-selective membranes reported in the literature varies across almost two orders of magnitude (see also [26]). Naturally, the performance of the membranes will have a very direct effect on the performance of the entire CSR process and the effect of different membrane permeabilities on the reactor performance is therefore important to quantify. It is also important to mention that good durability under moderately high-temperature fluidized bed operation is a prerequisite for application in the CSR process. This condition makes some of the high-permeability membranes reported in the literature unsuitable for the present study.

Five simulation experiments were completed on the finely resolved grid described in Section 3.2 in order to assess the influence of membrane permeability. Simulations were run isothermally (600 °C) and only catalytic reactions were included in order to achieve a clean comparison between cases. Cases were set up so that the gas feed rate was increased proportionally with the membrane permeability in order to assess whether any mass transfer or reaction rate limitations become applicable at higher flow rates. The cases are specified in Table 4.

Table 4: Five cases used to investigate the effect of membrane permeability. Membrane permeabilities were defined relative to the slowest case [17]. The fuel was fed at 600 °C with a H₂O:CH₄ ratio of 3:1.

<table>
<thead>
<tr>
<th>Feed velocity (m/s)</th>
<th>H₂ flux through membranes (relative to base case)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>1x</td>
</tr>
<tr>
<td>0.1</td>
<td>2x</td>
</tr>
<tr>
<td>0.2</td>
<td>4x</td>
</tr>
<tr>
<td>0.4</td>
<td>8x</td>
</tr>
<tr>
<td>0.8</td>
<td>16x</td>
</tr>
</tbody>
</table>
Results will be expressed in terms of four important performance measures for the CSR system:

- **H₂ recovery.** This measure simply expresses the fraction of H₂ recovered through the membranes relative to the total H₂ formed in the process and is therefore the most direct indication of membrane performance.
- **Overall H₂ recovery.** This measure is the fraction of H₂ recovered through the membranes relative to the theoretical maximum H₂ yield from the process (4x the CH₄ molar flow rate).
- **CO₂ selectivity.** Since it is important from an energy balance point of view to convert all carbon to CO₂, the CO₂ selectivity will be monitored as the fraction total carbon exiting the reactor as CO₂.
- **CH₄ conversion.** H₂ and CO exiting the reactor can be further processed downstream and it is therefore important to reform as much methane as possible.

These four performance measures are given below for the five cases detailed in Table 4.

![Graph showing reactor performance for different cases](image)

**Figure 2: Reactor performance for the different cases detailed in Table 4.**

It is clear that the reactor performance decreases as the fuel feed rate and membrane permeability are increased proportionally. This is an indication that some mass transfer and/or reaction rate limitations become significant at higher fuel feed rates. To check for the influence of reaction rate limitations, each simulation was run without membranes activated in order to assess whether equilibrium concentrations could be achieved within the gas residence time in the reactor. This would give a good indication of whether the reaction rates are limiting because the gas volume without H₂ extraction through the membranes is substantially higher, leading to shorter gas residence times.
As shown in Figure 3, the reaction rates are not limiting except for a small deviation from equilibrium concentrations in the case with the fastest fluidization. This indicates that the decrease in reactor performance shown in Figure 2 is primarily the result of mass transfer limitations due to concentration gradients developing in the reactor. This is shown in Figure 4 where it is clear that some radial H$_2$ concentration gradients develop at the higher flow rates.

These gradients develop as a result of the recirculatory flow pattern developing in the fluidized bed reactor. As a result, the gas slips through the centre of the bed, allowing less time for diffusion into the membranes and the associated beneficial shift in reaction equilibrium. In contrast, the gas in the downwards flowing regions of the bed (close to the walls) is afforded additional time to diffuse into the membranes. The result is a greater H$_2$ concentration at the centre of the bed and somewhat reduced reactor performance.

It is also possible that this effect would be significantly greater in a larger reactor where the bubble size is significantly smaller than the bed width. This situation could lead to increased radial volume fraction segregation and a greater mass transfer limitation. However, the presence of membranes (obstructions) should reduce this negative effect relative to a fluidized bed with no obstructions.
Figure 4: Instantaneous contours of the solids volume fraction (top) and the $H_2$ mole fraction (bottom) for the five different flow velocities and membrane permeation rates given in Table 4.
It is therefore clear that the membrane permeation rate implemented in the model can have a very large influence on reactor performance. For a given membrane surface area, the reactor throughput rate is not fully proportional to the permeability because of mass transfer limitations in the bed, but does increase substantially. Increased membrane permeability should therefore be a major research objective for improving the CSR process.

### 4.2 Full CSR cycle

Several full cycles consisting of subsequent air and fuel stages were completed in order to assess the transient behaviour of the CSR concept. The inlet conditions are given in Table 5 where the gasses were fed at roughly 10 times minimum fluidization velocity.

**Table 5: Inlet specifications for the CSR cycle.**

<table>
<thead>
<tr>
<th>Stage</th>
<th>Time (s)</th>
<th>Fluidization velocity (m/s)</th>
<th>Temperature (°C)</th>
<th>Composition (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>60</td>
<td>0.1</td>
<td>25</td>
<td>O₂: 21  N₂: 79</td>
</tr>
<tr>
<td>Fuel</td>
<td>60</td>
<td>0.13</td>
<td>110</td>
<td>CH₄: 33.33  H₂O: 66.67</td>
</tr>
</tbody>
</table>

A 0D model was used to estimate that the above conditions will result in an average reactor temperature in the range of 600 °C. A membrane permeation rate of 10 times that given in Equation 13 was used.

The most important outputs from the CSR cycle are given in Figure 5 to Figure 7.

![Figure 5: Average bed temperature and NiO mass fraction across the CSR cycle.](image)

The expected transient bed temperature variation is clearly shown in Figure 5. During the air stage, the oxygen carrier is oxidized to NiO and a significant amount of heat is generated through the highly exothermic oxidation reaction. This heat is then consumed during the fuel stage by the endothermic reduction (which consumes NiO) and reforming reactions.
Figure 6 shows complete O₂ conversion during the air stage, resulting in a pure N₂ outlet stream and minimal heat extraction by the cold air entering the reactor. During the fuel stage, clear trends of decreasing H₂O concentrations and increasing H₂ and CO concentrations can be observed. There is also a very small amount of CH₄ slip occurring towards the end of the fuel stage.

These trends are the result of the oxygen carrier becoming more reduced and the reduction reactions with CH₄, H₂ and CO becoming slower. As a result, less CH₄, H₂ and CO react directly with the NiO in the oxygen carrier, resulting in increased concentrations of these components.

As a result of the increasing H₂ concentrations in the reactor, both the H₂ extraction through the membranes and the H₂ in the retentate gas also increase as the fuel stage progresses (Figure 7). For perspective, the maximum amount of H₂ that can be produced by the system is also given in Figure 7. This is calculated as the sum of the H₂ extracted through the membranes and the H₂ in the retentate gas as well as the potential H₂ formation which equals the CO plus 4 times the CH₄ exiting the reactor. It is shown that H₂ recovery gradually decreases across the fuel stage as a result of increasing H₂ mole fractions which lessen the consumption of CO and CH₄ through the water-gas shift and steam-methane reforming equilibrium reactions.
Figure 7: Molar flow rate of hydrogen through the membranes and through the reactor outlet compared to the maximum recoverable amount of H₂.

Figure 6 also shows that the time during which N₂ and CO₂ mixes following a switch in the feed gases is very short. If the switch in the reactor outlet streams is made 2.5 s after the inlet switch is made, 2.5% of the CO₂ and 1.1% of the CO generated during the fuel stage escapes with the nitrogen stream. These percentages can be reduced substantially by increasing the stage times and converting the oxygen carrier to a higher degree. The trade-off is that this would result in a larger temperature variation across the cycle making process control and integration into a full plant more challenging.

A visual representation of the CSR cycle at three points during the cycle is given below.

Figure 8: Instantaneous contours of important flow variables at a time of 32.5 s (middle of the air stage). The ranges of the blue-to-red colour scale are given in brackets on each contour plot.

It is clear from Figure 8 that the oxidation reaction rate is easily fast enough to result in complete O₂ conversion (rightmost contour plot) even at 600 °C. This implies that the oxidation stage can potentially be carried out at a higher flow rate and a shorter stage time, thereby increasing the process throughput rate.
Figure 9 shows a small amount of mixing between CO$_2$ and N$_2$ (the blue regions in the H$_2$, H$_2$O, CO and CO$_2$ contour plots) directly after the switch in the feed gases is made. This mixing is limited by the small freeboard region and the limited back-mixing caused by the presence of membranes (obstructions). In practice, the size of the freeboard should be adjusted based on the particle elutriation rate desired to continuously replenish spent oxygen carrier material. This is a separate optimization exercise and will also influence the CO$_2$ separation efficiency of the process. If further increases in CO$_2$ separation efficiency are desired, a short steam purging stage can also be inserted between the air and fuel stages.

It is clear from Figure 10 that the heterogeneous and catalytic reactions are taking place simultaneously during the fuel stage. Some NiO is still present in the reactor and is continuously reduced by the CH$_4$ fuel as well as the H$_2$ and CO formed though the reforming reactions.

Given the trends in Figure 6 and Figure 7, a good topic for future investigation appears to be a gradual shift in the gas inlet composition with the CH$_4$ concentration gradually reducing across the fuel stage. In this way, the H$_2$O produced from the complete combustion of CH$_4$ would serve to drive the catalytic reactions at the start of the stage when the heterogeneous reactions are faster, while increasing amounts of H$_2$O fed towards the end of the fuel stage.
drives the catalytic reactions when the generation of H₂O through the heterogeneous reactions is very slow. This can minimize the steam feed rate required and result in a more constant H₂ output than the one shown in Figure 7.

5 Summary and conclusions

This paper presented an initial numerical investigation into the new process concept: Chemical Switching Reforming. This concept intensifies the three stages of hydrogen production; steam methane reforming, water-gas shift and H₂ purification, into a single reactor. The reactor contains hydrogen perm-selective membranes to produce pure H₂ and simultaneously shift produced CO into additional H₂. Using ideal membranes, the process can theoretically produce pure streams of H₂, CO₂ and N₂.

The membrane permeability was identified as the most important variable influencing process performance. Literature values of hydrogen perm-selective membrane performance vary over close to two orders of magnitude and this large variability will have a very direct influence on the performance of the process. Simulations revealed that higher membrane permeabilities allowed for greater fuel throughput, but that mass transfer limitations created by the radial volume fraction segregation within the bed become significant at higher fluidization velocities. Improved permeability is therefore an important future research topic for the CSR process, but the higher fuel throughputs achievable though better performing membranes will also make the reactor design exercise more challenging.

Finally, a complete CSR cycle was simulated to investigate the transient process performance of the CSR concept. It was shown that the oxidation reaction is sufficiently fast to ensure complete O₂ conversion, leading to a pure N₂ outlet stream and minimal heat extraction in the air stage. During the fuel stage, H₂ and CO formation gradually increased with time as the oxygen carrier became increasingly reduced. H₂ extraction through the membranes increased in a similar manner. An interesting topic for future research therefore appears to be transient adjustments in the feed composition (H₂O/CH₄ ratio) in order to achieve a more constant output of H₂ and to minimize steam consumption.

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7 References


