Measurement of solid circulation rate with optical and pressure transducer technique in circulating systems

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Colui che ama, fa tutto senza fatica,
oppure ama la sua fatica.
(Bernadette di Lourdes)

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Extend summary

Scope of the work:

The increase of CO₂ emissions of the last few years due to a huge utilization of fossil fuels and the related problem of global warming, has forced modern society to think about possible solutions to reduce the concentration of CO₂ in the atmosphere. One of these is to integrate CCS (Carbon capture and storage) systems in power plant generation in order to capture the CO₂ produced and store it in apposite sites. Anyway this solution decreases the efficiency of the plant and involves bigger costs. Another possibility is to use hydrogen as an alternative fuel with potential CO₂ emissions-free: the SMR (Steam methane reforming) process used today to produce most of the H₂, produces a big amount of CO₂, thus CCS have to be integrated also in hydrogen production plants.

The scope of the work is to analyze new systems of H₂ production with membrane reactors [9-11] that can represent a more efficient way to produce H₂ with low CO₂ emissions. Chemical looping [13-15] has been developed as an alternative way for hydrogen production with CO₂ capture. This technology is based on two reactors: an air reactor in which the oxidation of Nickel occurred and the fuel reactor in which the conversion of methane started. The term “Chemical-Looping” has been used for cycling processes that use a solid material as oxygen-carrier containing the oxygen required for the conversion of the fuel. To close the loop, the oxygen depleted solid material must be re-oxidized before to start a new cycle. An important improvement is been reached by this technology because of the autothermal operation that could be achieved in the CLR (Chemical looping reforming) instead of high external heat demand required in traditional SMR reactors.

The novel technology that has been studied is the Membrane Assisted-Chemical Looping Reforming (MA-CLR) [12] which consists on an air reactor and a fluidized bed membrane reactor (FBMR) as fuel reactor. Solid circulation rate is an important parameter for chemical looping system, since it help and control the heat flux from air reactor to fuel reactor influencing the methane conversion and hydrogen production.

The Membrane Assisted-Chemical looping reforming technology is based on the concept of chemical looping and it is shown in figure 1. In particular it combines the advantages of FBMR and CLR. The fuel reactor is a bubbling fluidized bed with membranes inside and it is fed with methane and steam at high pressure and temperature in the range of 500-700 °C. The steam methane reforming reaction can occur because the oxidized Nickel provide the oxygen required for the partial combustion of the fuel. In the fuel reactor a partial combustion of the fuel takes place and for this reason it is important to feed a shortage of oxygen in order to avoid complete combustion. The oxygen carrier is subsequently circulated to the air reactor where it is oxidized with air via an exothermic reaction and the hot regenerated material is ready to start a new cycle. In this way it is possible to have an auto-thermal process due to the partial combustion with the looping of the solid, avoiding external burners.
The scope of the work consists in studying the solid circulation rate for different operative conditions such as velocity in air and fuel reactor, particle type and size, solids inventory and sphericity. After this analysis, the fuel reactor is studied with modelling and experiments changing temperature, pressure, composition and velocities. The importance of this work consists on the possibility to understand better the behaviour of MA-CLR summing the information from the analysis of solid circulation rate and the study of FBMR. The purpose of analyse solid circulation rates and membrane fluidized bed reactor is to study before the heat flux going from air to fuel reactor and after the behaviour of membrane fluidized bed reactor compared to a simple fluidized bed reactor.

**Description of the proposed schemes:**

In order to study the effect of solid circulation rate on heat flux from air reactor to fuel reactor, a pilot plant with a design fuel power of 120 kW is examined. In a first moment, the real molar flux are used to check the heat flux going from air to fuel reactor and after the flux molar are changed, using the same temperature conditions and same reactor to show the behavior of the system when solid circulation rate is changed.

To study the solid circulation rate, a 2D reactor is used, that consists of 3 different vessels, one internal and concentric column and two external ones as it is possible to see in figure 2. The internal column is a riser reactor and represents the air reactor in Chemical looping systems, while the two external columns operated in the bubbling regime represent the fuel reactor in Chemical looping. The riser is 202 cm in height and 7.3 cm in width and operates in the fast fluidization regime. The riser is the driving force for the solids circulation and operates above the terminal velocity of the particles. Particles circulate from the top of the riser to the external columns, which are 7.0 cm in width. Solids circulate from the bottom of the external vessels to the riser through two orifices with an internal diameter of 1.5 cm placed 15.2 cm above the distributor of the central column.
The performance of the reactor is in high degree affected by the solid circulation rate between the riser and fuel columns. A stable solid circulation is required in Chemical looping processes to provide the right amount of oxygen and hence heat in the fuel reactor. In order to be able to describe the solid circulation rate in circulating systems, three different methods are available from literature. The collecting method that is the general one, optical technique, that was deeply studied for simply fluidized bed reactors in literature and pressure method, which results were not able to describe SCR accurately. To study this phenomenon in the novel pseudo 2D column, two windows with holes transferring particles from the riser to the fuel columns have been designed and installed. Particle collection is performed by driving out of the column the particles transferred from the riser column to the fuel columns. These windows are displayed in figure 3 and SCR can be obtained by measuring the time of solids accumulation.

The optical technique is based on recording images with a high speed camera and subsequently their analysis based on cross correlation methods. In this study a Dantec Dynamics Flowsense EO 16M camera is used for PIV-DIA analysis in the 2D column, which provides a maximum resolution of 4872 x 3248 pixels. A software package (Dynamic Studio) is used to adjust the settings of the recordings and post process the pictures. Pictures are taken in double frame mode, two images are taken with a very short interval of 0.5 ms, followed by a longer interval of 0.5 s before the next two pictures are recorded. In this way, the two consecutive images can be analyzed together in order to get the information of the hydrodynamics of the bed. As depicted in figure 4, two LED lights are used for illuminating the bed, always providing that homogeneous illumination is achieved. A trigger connected to the computer controls the camera shutter and a resolution of 3 pixels per particle is used during the recordings, always at 8 bits depth for double frame mode.
The main advantage of this system is that real SCR are known by collecting particles, thus optimization can be done for this technique. PIV analysis only provides information on the particle velocities. To determine the solid flux profiles another post-processing technique is used on the recorded images: Digital Image Analysis (DIA). DIA is an in-house software developed with the image processing toolbox in Matlab. In this technique, image is divided into interrogation zones where the normalized pixel intensity in each zone is used as primarily tool to get the bed porosity. The values obtained represent the results of 2D solids fraction measurements, which are used to predict 3D behavior of bed. In this case the 2D pixel intensity is correlated to 3D porosity using the correlation suggested by de Jong et al [1], which was developed for fluidized beds. However, solids hold-up in this system are much lower than in fluidized beds, thus a new correction method from planar 2D intensities to reliable 3D solids hold up has been developed in this work.

In the previous work of Jong, solid circulation rate was studied for FBR and the equation (1) was found.
\[
\begin{align*}
\varepsilon_{3D} &= \begin{cases} 
A \frac{\varepsilon_{2D}}{1 - \frac{1}{B}\varepsilon_{2D}} & \text{for } \varepsilon_{3D} < \varepsilon_{3D,max} \\
\varepsilon_{3D,max} & \text{for } \varepsilon_{3D} \geq \varepsilon_{3D,max}
\end{cases} \quad (1)
\end{align*}
\]

Where \(A\) and \(B\) are parameters influencing the initial and final slope of the curve, while \(\varepsilon_{2D}\) is the 2D porosity, and \(\varepsilon_{3D}\) is the real one and it is described in figure 5.

Figure 5 Correlation connecting porosity 2D to porosity 3D

Table 1 Influence of bed depth on A and B parameters

<table>
<thead>
<tr>
<th>Particle diameter [μm]</th>
<th>u/umf</th>
<th>Δz/dp</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>3</td>
<td>6</td>
<td>0,097</td>
<td>0,999</td>
</tr>
<tr>
<td>500</td>
<td>3</td>
<td>6</td>
<td>0,098</td>
<td>1,005</td>
</tr>
<tr>
<td>1000</td>
<td>3</td>
<td>6</td>
<td>0,098</td>
<td>1,007</td>
</tr>
<tr>
<td>500</td>
<td>3</td>
<td>6</td>
<td>0,098</td>
<td>1,005</td>
</tr>
<tr>
<td>500</td>
<td>3</td>
<td>12</td>
<td>0,05</td>
<td>0,935</td>
</tr>
<tr>
<td>500</td>
<td>3</td>
<td>20</td>
<td>0,024</td>
<td>0,885</td>
</tr>
<tr>
<td>500</td>
<td>3</td>
<td>30</td>
<td>0,021</td>
<td>0,882</td>
</tr>
<tr>
<td>100</td>
<td>3</td>
<td>6</td>
<td>0,0097</td>
<td>0,999</td>
</tr>
<tr>
<td>100</td>
<td>6</td>
<td>6</td>
<td>0,1</td>
<td>1,006</td>
</tr>
<tr>
<td>100</td>
<td>10</td>
<td>6</td>
<td>0,1</td>
<td>1,013</td>
</tr>
</tbody>
</table>

The relative bed depth \(\Delta z/d_p\) is expected to affect the parameters \(A\) and \(B\) as the table 1 shows, but printout \(A\) and \(B\) are good only for FBR because in chemical looping and riser, the maximum porosity decreases and the curve is moved under. The parameter values from table are not suitable for this case because they were calculated for a fluidized bed reactor and not for a diluted system like the ICFB reactor. The most important
parameter affecting A and B is the bed depth meanwhile a change in particle size and u/umf give similar results of A and B. With Δz/dₚ higher than 20, there is a vertical asymptote in the curve. For the all cases considered in the experiments the bed depth is always higher than 20.

Before the relationship from 2D to 3D hold up is proposed, inhomogeneous lighting in the different set of experiments is corrected. Due to in the window for PIV/DIA the fuel columns show a much lower particle hold up, they might be more affected by inhomogeneous lighting as compared to the riser column, thus the main correction procedure is performed in these columns. To correct for it, the bed is filled with particles and images are taken to the fixed bed, which is subsequently used as background for normalization of every single image of the experiment. In this method the lighting for the background image and the corresponding to the experiments should exactly the same, it means the camera and LED light should be exactly in the same position.

![Figure 6. Intensity profiles in the right fuel column for two different recordings using the same experimental conditions before and after background correction](image)

Both histograms correspond to operation conditions of the same experiment but with completely different initial illuminations. In figure 6, it is observed how for different illuminations, the fixed bed background correction method is able to normalize the intensities, which would lead to reproducibility of the measurements. For the riser vessel, which is less diluted than the fuel vessels, the background image used for the correction of inhomogeneous lighting is obtained by averaging all images of the recorded experiment, which represents a dynamic background determination. Subsequently, every image is normalized by the subtraction of this average background image. Once images have been normalized and corrected by inhomogeneous lighting, a reliable correlation between the pixel intensity (2D solids fraction) and the actual porosity (3D solids fraction) is required. In such diluted systems like the ICFBR, a linear correlation between the intensity and porosity is proposed in equation (1).

\[ \varepsilon_{3D} = A \cdot \varepsilon_{2D} \]  

The third method aims at determining the total pressure drop in the riser (\( \Delta P_{\text{riser}} \)) between the top and bottom parts of the column. This method allows the estimation of the solids circulation rates in the riser as a function of the local solids holdup measured. For a proper measurement of SCR using the pressure drop method is important the location of the pressure transducers in order to get a good description of the behaviour of the bed. These pressure transducers have been located at specific positions in the bed.
The method is based on the determination of solids circulation rates from the particle velocity and solids holdup according to the equation (2).

\[ SCR = u_P \cdot \varepsilon_S \cdot A_c \cdot \rho_s \quad (2) \]

A new method is carried on in this work in order to measure the solid circulation rate only knowing the pressure drop between the top and the bottom of the system. Since all the pressure methods available in literature give an error in the range between 30-60%, a new procedure is developed in the work. This new method consist on the Bernoulli equation for riser and on the Richardson and Zaki equation, described in equations (3) and (4).

\[
\begin{aligned}
\{ \\
up &= \frac{u_g}{(1 - \varepsilon_S)} - u_t \cdot (1 - \varepsilon_S)^{n-1} \\
p_2 - p_1 &= \frac{\rho_R}{\rho_g} \cdot g \cdot (h_2 - h_1) = 4 \cdot F \cdot \frac{L}{D} \cdot \frac{1}{2} \cdot (u_g + u_p)^2
\end{aligned}
\quad (3)
\]

After the analysis of solid circulation rate, the attention is focused on fuel reactor that is examined with modelling and experiments in order to compare membrane fluidized bed reactors and fluidized bed reactors.

The modelling is based on Delphi 7 and all the information regarding it can be found in the work by Gallucci at al [30]. The reactor has a diameter equal to 0,045 m and a height of 0,17 m. The distance distributor to the beginning of the membrane is equal to 3 cm. The conditions for the catalyst used, that is activated nickel, are described in table 1 while for the membrane in table 2.

### Table 1 Operative parameters for catalyst

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>particle diameter</th>
<th>density</th>
<th>particle porosity</th>
<th>apparent density</th>
<th>surface area</th>
<th>sphrecty factor</th>
<th>amount</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.00025</td>
<td>3450</td>
<td>0.404</td>
<td>1394</td>
<td>102000</td>
<td>0.75</td>
<td>0.3</td>
</tr>
</tbody>
</table>
Table 2 Operative parameters for membrane

<table>
<thead>
<tr>
<th>Membrane</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>0,01</td>
<td>m</td>
</tr>
<tr>
<td>Length</td>
<td>0,13</td>
<td>m</td>
</tr>
<tr>
<td>Thickness</td>
<td>0,000005</td>
<td>m</td>
</tr>
<tr>
<td>Pm</td>
<td>4,24E-10</td>
<td>mol/s/m/Pa^{0.74}</td>
</tr>
<tr>
<td>Ea</td>
<td>5,81</td>
<td>kJ/mol</td>
</tr>
<tr>
<td>n</td>
<td>0,74</td>
<td>(-)</td>
</tr>
</tbody>
</table>

The purpose of this analysis is to study the methane conversion and hydrogen production in FBR and MFBR changing temperature, pressure, velocity and composition of the system.

**Final results and conclusions:**

For optical technique, it was possible to find the same value of A that can connect the 2D to the 3D porosity for different superficial gas velocity, particles type, size, solids inventory and sphericity. As already said, for all the cases considered, the bed depth is always higher than 20 and it can explains the fact that A is the same for different operating conditions.

The value obtained of A in the fuel columns is 0.049, whereas in the riser column, where not a fixed bed background image is used but a dynamic background instead, the encountered value of A is 0.032. The fact that a different value is obtained is related to the background image, which is different for the two cases. As observed from the results the SCR can be well predicted using this method. This method has been successfully applied for spherical particles, whereas it also gives good estimations for non-spherical particles, which are most likely used at industrial scale. The pressure drop and the optical methods have in common that are relatively cheap and that after first calibration (for the optical technique), maintenance is not extensively required.

![Figure 7. Parity plot for SCR measured using PIV/DIA and pressure drop methods compared to SCR determined experimentally by collecting particles and their deviation.](image)

Figure 7. Parity plot for SCR measured using PIV/DIA and pressure drop methods compared to SCR determined experimentally by collecting particles and their deviation.
In this work, both the optical and pressure methods are innovative and applicable with good results for fluidized bed reactors in chemical looping. Both this methods are able to describe solid circulation rate with a small deviation compared to collecting particles. SCR measured with the three methods, including also the collecting particles that is the reference method, lead to similar results within 20 % of maximum deviation and most of them within 10 % as it is possible to see in figure 7.

For the studying of fuel reactor, it was possible to find good correspondence from experimental results and modelling prediction and the main result consists on the fact that membrane fluidized bed reactor gives always better conversion compared to a simple fluidized bed reactor.

A possible important study that should be carried on, consists on the possibilities to extend the analysis related to methane conversion and hydrogen production observing the influence of temperature, pressure, velocity and composition on the membrane assisted chemical looping reforming. This system is quite innovative because of the possibility to produce pure hydrogen, in an autothermal way and with CO2 capture. It should be interesting to couple the information of SCR into the model to simulate the MA-CLR with two reactors and also to verify the findings at high temperature and under reactive conditions.
Riassunto esteso

Scopo del lavoro

L’aumento delle emissioni di CO₂ degli ultimi anni dovuto ad un intenso utilizzo di combustibili fossili e i conseguenti problemi legati al riscaldamento ambientale, hanno portato le società moderne a cercare possibili soluzioni per ridurre la concentrazione di CO₂ in atmosfera. Una possibile soluzione consiste nell’integrare sistemi CCS (Capture carbon and storage) negli impianti di generazione di potenza per poter catturare la CO₂ prodotta e stoccarsia in appositi siti. L’aspetto negativo di questa soluzione consiste nella diminuzione dell’efficienza dell’impianto e nei maggiori costi legati ad esso. Un’ulteriore possibilità è quella di utilizzare l’idrogeno come fonte alternativa che potenzialmente non emette CO₂: i processi di SMR (Steam methane reforming) producono una grande quantità di idrogeno ma con elevate emissioni di CO₂, inoltre i sistemi CCS devono essere integrati anche negli impianti per la produzione di idrogeno.

Lo scopo di questo lavoro consiste nell’analizzare nuovi sistemi di produzione di H₂ con reattori a membrana che possano rappresentare un metodo più efficiente per produrre idrogeno con basse emissioni di CO₂.

Il chemical looping è un sistema alternativo per la produzione di idrogeno con cattura di CO₂. Questa tecnologia prevede due reattori: il primo è l’air reactor in cui avviene l’ossidazione del Nickel mentre il secondo è il fuel reactor in cui si verifica la reazione di steam reforming e quindi la conversione del metano. Il termine chemical looping è stato utilizzato per riferirsi a processi ciclici che utilizzano un materiale solido come portatore di ossigeno che contiene l’ossigeno necessario per la conversione del combustibile. Inoltre per chiudere il ciclo, quando il materiale solido ha esaurito l’ossigeno deve essere ossidato nuovamente prima di tornare ancora nel fuel reactor. Questa tecnologia prevede un importante vantaggio che consiste nell’operazione autotermica che può essere raggiunta nel CLR (Chemical looping reforming) sostituiva dell’elevata quantità di energia richiesta nei sistemi tradizionali di SMR.

Un’ulteriore tecnologia innovativa che è stata oggetto di studio in questa analisi, consiste nel Membrane Assisted-Chemical Looping Reforming (MA-CLR) che è costituito dall’air reactor e dal fluidized bed membrane reactor (FBMR). La quantità di solido che circola tra i due reattori, è un parametro importante nel chemical looping dal momento che influenza e controlla la quantità di energia che passa dall’air reactor al fuel reactor condizionando la conversione di metano e la produzione di idrogeno.

La tecnologia del Membrane Assisted-Chemical looping reforming si basa sul concetto del chemical looping come è possibile vedere in figura 1, dove viene descritto lo schema d’impianto. In particolare combina i vantaggi del FBMR e CLR. Il fuel reactor è un reattore a letto fluidizzato con membrana che viene alimentato con metano e vapore ad alta pressione e temperatura in un range tra 500-700 °C. Lo SMR può avvenire perché la potenza richiesta è fornita dalla parziale ossidazione del metano, garantita dalla circolazione del nickel ossidato. Nel fuel reactor avviene la combustione parziale e per questo motivo è importante alimentare una ridotta quantità di ossigeno in modo che si eviti la completa combustione del metano. Un importante vantaggio riguarda la possibilità di evitare costosi sistemi di separazione dell’ossigeno dall’aria, che nel chemical looping viene direttamente separata grazie all’air reactor in cui l’ossigeno si lega al metallo e al ciclone che espelle i materiali non solidi.

Il vettore di ossigeno circola dall’air reactor dove è ossidato con aria tramite una reazione esotermica in modo che il materiale solido possa incominciare un nuovo ciclo. In questo modo è possibile avere un processo autotermico evitando l’utilizzo di bruciatori esterni, grazie alla parziale combustione del metano, resa possibile dalla circolazione di solido.

Lo scopo del lavoro consiste nello studiare la circolazione di solido sotto differenti condizioni operative, quali la velocità del gas nell’air e fuel reactor, il tipo di particelle, la dimensione, la quantità di solido e la sfericità...
delle particelle. Dopo questa analisi, lo studio è stato focalizzato sul fuel reactor, con lo scopo di comparare esperimenti e modellazione per verificare come la temperatura, la pressione, la composizione e la velocità possano influire sulla conversione di metano e la produzione di idrogeno.

![Configurazione del membrane assisted chemical looping reforming](image)

**Figura 1 Configurazione del membrane assisted chemical looping reforming**

L’importanza di questo lavoro consiste nella possibilità di capire a fondo il comportamento del MA-CLR che è composto da due reattori: air e fuel reactor e in particolare quest’ultimo è un reattore fluidizzato con membrana. L’interesse di questa analisi è quello di poter predire la circolazione di solido nel chemical looping perché influenza il fuel reactor e di studiare il comportamento del reattore a membrana per poter trovare i vantaggi di un sistema circolante con membrana.

**Descrizioni degli schemi proposti:**

Per studiare la circolazione di solido, è stato utilizzato un reattore 2D costituito da tre colonne, una interna e due esterne, come è possibile vedere nella figura 2. Il vessel interno è un riser che rappresenta l’air reactor nel chemical looping. Tale reattore è alto 202 cm e largo 7.3 cm e opera nel regime di fluidizzazione veloce.

Il riser è la forza motrice del solid circulation rate e opera sopra la velocità terminale delle particelle. Le particelle circolano dalla parte superiore del riser alle colonne esterne che sono larghe 7 cm. Il solido inoltre passa dalla parte inferiore dei fuel reactors, tramite due fori di diametro interno pari a 1.5 cm posti a 15.2 cm sopra il distributore della colonna centrale.
La prestazione del reattore è altamente influenzata dalla circolazione di solido tra il riser e il fuel reactor. Una stabile circolazione di solido è richiesta nel chemical looping per poter garantire la corretta quantità di ossigeno e quindi di potenza termica al fuel reactor. Per poter analizzare questo fenomeno, è stato utilizzato un reattore innovativo e pseudo 2D costituito da due finestre con fori che permettono il passaggio di particelle dal riser al fuel reactors. Per poter studiare la circolazione di solido, sono stati impiegati tre metodi differenti: la collezione delle particelle che viene utilizzato come riferimento, il metodo ottico e quello basato sui trasduttori di pressione.

La collezione delle particelle è garantita dalla presenza di due finestre localizzare nei fuel reactors, come è possibile vedere in figura 3, in modo che le particelle che si muovono dal riser alle fuel columns, possono essere raccolte nel momento in cui escono dalle finestre presenti. La circolazione di solido, può essere ottenuta pesando la quantità di particelle e misurando il tempo di accumulazione del solido.

Le misure ottiche si basano su un metodo che consiste nello scattare immagini con una camera ad alta velocità, e successivamente analizzarle tramite un metodo che si basa su una correlazione incrociata. Per l’analisi PIV-DIA, è stata utilizzata una camera Dantec Dynamics Flowsense EO 16M, che ha una massima risoluzione di 4872 x 3248 pixels. Successivamente le immagini sono processate tramite il software Dynamic Studio. Le immagini sono ottenute in modalità double frame dal momento che due immagini sono scattate con un tempo di intercorrenza di 0,5 ms e susseguite da un intervallo più lungo di 0,5s prima che le due immagini successive siano riprese. In questo modo, è possibile ottenere informazioni sull’idrodinamica del letto utilizzando le due immagini immediatamente consecutive. Come mostrato in figura 4, sono utilizzate due luce LED per illuminare il letto in modo da garantire un’illuminazione omogenea. Un trigger connesso al computer controlla la camera e una risoluzione di 3 pixels per particella è usata durante la ripresa delle immagini, sempre a 8 bits di profondità for immagine double frame.
Il principale vantaggio di questo sistema è che il valore reale del SCR è conosciuto dal metodo basato sul collezionare le particelle in modo che un'ottimizzazione possa essere fatto per questa tecnica. L’analisi PIV dà informazioni sulla velocità delle particelle. Il profilo della portata di solido è ottenuto tramite un’altra tecnica di elaborazione: Digital Image Analysis (DIA). DIA è un software proprietario della Tue University sviluppato in Matlab per processare le immagini. In questa tecnica, l’immagine viene divisa in zone interrogative per calcolare un’intensità normalizzata che rappresenta la porosità del letto. I valori ottenuti rappresentano una porosità 2D, che vengono utilizzati per ricavare la reale porosità del reattore, tramite una correlazione indicata da Jong in [1], che fu sviluppata per i reattori a letto fluidizzato. Comunque, la porosità del solido in questi sistemi è molto inferiore rispetto ai letti fluidizzati e per questo motivo è stata sviluppata in questo lavoro, una nuova correlazione che connette l’intensità 2D alla reale porosità 3D.
Nel precedente lavoro di Jong, la quantità di solido circolante tra i due reattori per un sistema a letto fluidizzato, era stato descritto tramite l’equazione (1).

\[
\begin{align*}
\varepsilon_{3D} &= \left\{ \begin{array}{l}
\frac{A \varepsilon_{2D}}{1 - \frac{1}{B} \varepsilon_{2D}} \quad \text{for} \quad \varepsilon_{3D} < \varepsilon_{3D,max} \\
\varepsilon_{3D,max} \quad \text{for} \quad \varepsilon_{3D} \geq \varepsilon_{3D,max}
\end{array} \right. \\
\end{align*}
\]

(1)

Dove A e B sono i parametri che influenzano l’inclinazione iniziale e finale della curva descritta in figura 5, mentre \(\varepsilon_{2D}\) è la porosità 2D, e \(\varepsilon_{3D}\) è quella reale del reattore.

**Figura 5** Correlazione che collega la porosità 2D a quella 3D

**Tabella 1** Influenza dello spessore del letto sui parametri A e B

<table>
<thead>
<tr>
<th>Particle diameter [μm]</th>
<th>u/umf</th>
<th>Δz/dp</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>3</td>
<td>6</td>
<td>0,097</td>
<td>0,999</td>
</tr>
<tr>
<td>500</td>
<td>3</td>
<td>6</td>
<td>0,098</td>
<td>1,005</td>
</tr>
<tr>
<td>1000</td>
<td>3</td>
<td>6</td>
<td>0,098</td>
<td>1,007</td>
</tr>
<tr>
<td>500</td>
<td>3</td>
<td>6</td>
<td>0,098</td>
<td>1,005</td>
</tr>
<tr>
<td>500</td>
<td>3</td>
<td>12</td>
<td>0,05</td>
<td>0,935</td>
</tr>
<tr>
<td>500</td>
<td>3</td>
<td>20</td>
<td>0,024</td>
<td>0,885</td>
</tr>
<tr>
<td>500</td>
<td>3</td>
<td>30</td>
<td>0,021</td>
<td>0,882</td>
</tr>
<tr>
<td>100</td>
<td>3</td>
<td>6</td>
<td>0,0097</td>
<td>0,999</td>
</tr>
<tr>
<td>100</td>
<td>6</td>
<td>6</td>
<td>0,1</td>
<td>1,006</td>
</tr>
<tr>
<td>100</td>
<td>10</td>
<td>6</td>
<td>0,1</td>
<td>1,013</td>
</tr>
</tbody>
</table>
Il rapporto tra la profondità del reattore e il diametro delle particelle utilizzate, è un parametro che può influenzare notevolmente A e B, come mostrato in tabella, ma i valori tabulati di A e B sono validi solo per reattori a letto fluidizzato, dal momento che nel chemical looping e nel riser, il grado di pieno diminuisce e quindi la curva è traslata verso il basso. Il principale parametro che influenza A e B è il rapporto $\Delta z/d_p$, mentre la dimensione della particella e il rapporto tra la velocità superficiale del gas e quella di minima fluidizzazione, garantiscono risultati simili dei valori A e B. Quando $\Delta z/d_p$ è maggiore di 20, si presenta un asintoto verticale nella curva. Per tutti i casi considerati negli esperimenti svolti, il rapporto tra la profondità e il diametro della particella, è sempre maggiore a 20.

Prima di poter utilizzare tale correlazione, è stato necessario correggere l’illuminazione nei differenti esperimenti elaborati. Dal momento che le colonne del fuel reactor mostrano una porosità decisamente inferiore, sono maggiormente influenzabili da una differente illuminazione rispetto al riser, per questo motivo, la principale correzione viene effettuata in quelle colonne. Per poter correggere possibili disomogeneità dovute al fatto che mantenere le luci nelle stesse posizioni per ogni caso effettuato era ampiamente difficoltoso, il letto è stato riempito completamente di particelle fino ad ottenere un letto fisso e le immagini ottenute sono state utilizzate come background per normalizzare ogni singola immagine degli esperimenti. Con questo metodo l’illuminazione per l’immagine di background e per le immagini degli esperimenti corrispondenti è esattamente la stessa, dato che le luci LED e la camera sono state mantenute accuratamente nella stessa posizione per ogni singolo esperimento.

![Figura 6. Profilo dell’intensità dei pixel nella colonna destra per due condizioni differenti dello stesso esperimento prima e dopo la correzione di background](image)

Entrambi gli istogrammi rosso e verde, corrispondono alle condizioni operative dello stesso esperimento ma con illuminazioni iniziali completamente differenti. In figura 6 è possibile osservare che il metodo del background ottenuto con letto fisso è in grado di normalizzare le intensità garantendo la riproducibilità degli esperimenti pur partendo da una differente illuminazione iniziale. Essendo il riser meno diluito rispetto ai fuel reactors, la correzione della disomogeneità di illuminazione con il metodo del background è ottenuto dalla somma della media di tutte le immagini consecutive che costituiscono la correzione dinamica del background.

Successivamente ogni immagine è normalizzata sottraendo l’immagine di background a quella originale. Una volta che l’immagine è stata normalizzata e corretta, è necessario ricorrere ad una correlazione che connetta l’intensità 2D alla reale porosità 3D. In questi sistemi diluiti come gli internal circulating fluidized bed reactors, è proposta una correlazione lineare, come è possibile vedere con l’equazione (1).
Il terzo metodo per calcolare la quantità di solido circolante si basa sulla determinazione della pressione totale nel riser tra la parte alta e bassa della colonna. Questo metodo permette di stimare la circolazione di solido nel riser come funzione della porosità della particella. Per un’appropriata misurazione del solido, nel metodo basato sui trasduttori di pressione è importante la posizione dei trasduttori in modo da ottenere un’accurata descrizione del comportamento del letto. I trasduttori di pressione sono collocati in posizioni specifiche, come è possibile vedere in figura (2).

Il metodo è basato sulla determinazione della quantità di solido circolante dalla velocità delle particelle e porosità tramite l’equazione (2).

$$SCR = u_p \cdot \varepsilon_S \cdot A_c \cdot \rho_s \quad (2)$$

E’ stato sviluppato un nuovo metodo per poter predire il solid circulation rate, conoscendo solo la differenza di pressione tra la parte superiore e inferiore del sistema. Dal momento che tutti i metodi utilizzati precedentemente in letteratura prevedevano un margine di errore compreso tra il 30-60%, è stata sviluppata una nuova procedura in questo lavoro. Questo approccio è basato sulle equazioni di Bernoulli e Richardson e Zaki descritte nelle equazioni (3) e (4).

$$u_p = \frac{u_g}{(1 - \varepsilon_S)} - u_t * (1 - \varepsilon_S)^{n-1} \quad (3)$$

$$\frac{p_2 - p_1}{\rho_R} - g * (h_2 - h_1) = 4 * F * \frac{L}{D} * \frac{1}{2} * (u_g + u_p)^2 \quad (4)$$

Dopo l’analisi riguardante il solid circulation rate, l’attenzione è stata focalizzata sullo studio del fuel reactor che viene esaminato tramite modellazione ed esperimenti per poter confrontare il reattore a letto fluidizzato con il membrane fluidized bed reactor.

La modellazione è effettuata con Delphi 7, le cui informazioni sono reperibili nel lavoro di Gallucci in [30]. Il reattore ha un diametro di 0,045 m ed un altezza di 0,17 m. La distanza del distributor dall’inizio della membrana è pari a 0,03 m. Le condizioni per il catalizzatore sono descritte in tabella 1 e per la membrana in tabella 2.

### Tabella 1 Parametri operative per il catalizzatore

<table>
<thead>
<tr>
<th>Catalyst</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>particle diameter</td>
<td>0,00025</td>
<td>M</td>
</tr>
<tr>
<td>density</td>
<td>3450</td>
<td>kg/m³</td>
</tr>
<tr>
<td>particle porosity</td>
<td>0,404</td>
<td>(-)</td>
</tr>
<tr>
<td>apparent density</td>
<td>1394</td>
<td>kg/m³</td>
</tr>
<tr>
<td>surface area</td>
<td>102000</td>
<td>m²/kg</td>
</tr>
<tr>
<td>sphrecty factor</td>
<td>0,75</td>
<td>(-)</td>
</tr>
<tr>
<td>amount</td>
<td>0,3</td>
<td>Kg</td>
</tr>
</tbody>
</table>
La pagina riporta la tabella 2 di parametri operativi per la membrana, con i seguenti dati:

<table>
<thead>
<tr>
<th>Membrane</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>0,01</td>
<td>M</td>
</tr>
<tr>
<td>Length</td>
<td>0,13</td>
<td>M</td>
</tr>
<tr>
<td>Thickness</td>
<td>0,000005</td>
<td>M</td>
</tr>
<tr>
<td>Pm</td>
<td>4,24E-10</td>
<td>mol/s/m/Pa^0.74</td>
</tr>
<tr>
<td>Ea</td>
<td>5,81</td>
<td>kJ/mol</td>
</tr>
<tr>
<td>n</td>
<td>0,74</td>
<td>(-)</td>
</tr>
</tbody>
</table>

Lo scopo di questa analisi è quello di capire come la variazione di parametri operativi quali temperatura, pressione, velocità e composizione, possano influenzare la conversione di metano e la produzione di idrogeno nel reattore a letto fluidizzato e nel MFBR.

**Risultati finali e conclusioni:**

Con il metodo ottico, variando la velocità superficiale del gas, il tipo di particella, la dimensione, la quantità di solido e la sfericità, si è trovato lo stesso valore di A nella correlazione tra l’intensità 2D e la porosità 3D per tutti i casi analizzati. Come già detto, quando il rapporto tra la profondità del reattore e il diametro delle particelle è maggiore di 20, nella curva in figura 5 si incontra un asintoto orizzontale, questo può spiegare il fatto che il valore di A resti sempre costante in tutti i casi considerati.

Il valore di A ottenuto nel fuel reactor è 0.049 mentre nel riser, dove al posto del background con letto fisso è utilizzata la correzione di background dinamico, il valore riscontrato è pari a 0.032 per tutti gli esperimenti svolti. Il fatto che si ottenga un valore differente è legato alla diversità di metodi impiegati per la correzione del background. Come è possibile osservare dai risultati in figura 7, il SCR può essere predetto in maniera accurata con il metodo ottico. Questo metodo è stato applicato con successo alle particelle sferiche, inoltre è in grado di dare risultati positivi anche per particelle non sferiche che sono per lo più utilizzate su scala industriale.

Il metodo dei trasduttori di pressione è in grado di misurare in maniera accurata la circolazione di solido per particelle sferiche, mentre risulta meno preciso per quanto riguarda le particelle non sferiche. Infatti la velocità terminale delle particelle può essere notevolmente influenzata dalla sfericità, quindi se i campioni di particelle non presentano la stessa identica sfericità, la velocità terminale può essere differente e questo comporterebbe una fluttuazione di pressione che fa deviare l’accuratezza delle misurazioni. Sia il metodo dei trasduttori di pressione sia quello ottico, hanno in comune il vantaggio di essere economici e, dopo la prima calibrazione, non richiedono particolari manutenzioni.
Figura 7. Risultati per SCR misurato con il metodo PIV/DIA e di pressione confrontato al SCR ottenuto sperimentalmente dal collecting particles e loro deviazioni assolute.

Da ciò che è stato esposto, si evince che entrambi i metodi sono innovativi e mostrano buoni risultati per la descrizione del solid circulation rate nei reattori a letto fluidizzato per sistemi circolanti. I risultati ottenuti con questi metodi, confrontati con il collecting particles, che è il metodo di riferimento, conducono a risultati che hanno una massima deviazione del 20% anche se la maggior parte di essi presenta una deviazione intorno al 10%, come è possibile vedere in figura 7.

Per l’analisi del fuel reactor, si è trovata una buona corrispondenza tra i risultati sperimentali e di modellazione. La constatazione principale consiste nel fatto che il membrane fluidized bed reactor presenta una conversione di metano maggiore rispetto al semplice reattore a letto fluidizzato.

Un possibile studio futuro consiste nell’estendere l’analisi relativa alla conversione di metano e produzione di idrogeno osservando l’influenza di temperatura, pressione, velocità e composizione sul MA-CLR. Questo sistema è innovativo, dal momento che può produrre idrogeno puro in maniera autotermica e con cattura di CO₂. Potrebbe inoltre essere interessante utilizzare le informazioni ottenute dallo studio del SCR per verificare sperimentalmente e con simulazione come la potenza richiesta al fuel reactor sia influenzata dalla quantità di solido circolante per il reattore MA-CLR.
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Abstract:

Chemical Looping Reforming for hydrogen production has been proposed as an efficient system that integrates CO₂ capture. This system avoids direct mixing of air and fuel and higher efficiencies are achieved. This novel technology is based on the circulation of a solid within two different reactors operated at different conditions. The solids circulation rates determine the well performance of the reactor concept. However, its prediction is not straightforward and many different techniques have been used in the literature. In this work a comparison of three different techniques is given. A pseudo 2D chemical looping system has been used to measure SCR using optical techniques, pressure transducers and particles collection. The three methods have been evaluated under different experimental conditions by varying superficial gas velocities, particle diameter and particle type. Results show that the SCR can be well predicted with optical and pressure drop methods by comparison to the collected amount of particles for both spherical particles and non-spherical particles. The fact that the optical and pressure methods are not intrusive represents the main advantage for both systems. Moreover, through the optical technique a better distribution of the solids hold-up along the riser of the chemical looping system has been determined. Furthermore, the pressure drop technique could be extrapolated to 3D high temperature systems for the prediction of SCR. Moreover in this work the comparison between fluidized bed reactor and membrane fluidized reactor is carried on both with modelling and experiments. The studying is doing changing operative conditions such as temperature, pressure, composition and velocity. The work shows a good correspondence between modelling and experiments for all the cases analyzed and it is possible to see that the methane conversion is higher for all the cases in MFBR. In this study, before the SCR is analyzed in order to understand the behavior of air reactor in chemical looping and after in order to sum the information the fuel reactor is analyzed, with a particular interest in MA-CLR that is composed of air reactor and membrane fluidized bed reactor.

Keywords: Circulating fluidized bed reactor, PIV/DIA, pressure sensors, Solids circulation rate, fluidized bed reactor, membrane fluidized bed reactor and Membrane assisted chemical looping reforming.
Il Chemical Looping Reforming, è un sistema efficiente per la produzione di idrogeno che consente la cattura di CO₂. Questo sistema inoltre impedisce il diretto miscelamento tra aria e combustibile per poter raggiungere elevate efficienze. Questa tecnologia si basa sulla circolazione di solido tra due differenti reattori che operano a condizioni differenti. La quantità di solido che circola determina il comportamento dei reattori. Comunque conoscere con esattezza la quantità di solido che circola non è semplice e molte tecniche sono state studiate in letteratura. In questo lavoro è stato fatto un confronto di tre metodi differenti. Per misurare la quantità di solido tra i due reattori, è stato utilizzato uno pseudo reattore 2D che permettesse tecniche ottiche, di pressione e di collezione delle particelle. I tre metodi sono stati validati utilizzando differenti condizioni sperimentali variando la velocità superficiale del gas, il diametro delle particelle e il tipo di particelle. I risultati mostrano che la quantità di solido circolante può essere predetto in maniera accurata sia per particelle sferiche che non sferiche, tramite i metodi ottici e di pressione confrontandoli con la tecnica di collezione delle particelle. Il principale vantaggio di entrambi i metodi risiede nel fatto che entrambe le tecniche sono non intrusive. Comunque grazie al metodo ottico, è stato possibile determinare l'andamento della distribuzione della porosità nel letto lungo il riser del chemical looping. L'importanza della tecnica che sfrutta la differenza di pressione, consiste nella possibilità di estendere il metodo ad un sistema 3D ad alta temperatura. Inoltre in questo lavoro è stato svolto un confronto tra reattore a letto fluidizzato e reattore a letto fluidizzato con membrana, sia sperimentalmente che con modellazione. Lo studio è stato fatto cambiando condizioni operative quali temperatura, pressione, composizione e velocità. Il lavoro mostra una buona corrispondenza tra modello e esperimenti per tutti i casi analizzati oltre ad evidenziare una miglior conversione di metano nel caso di reattore a membrana per ognuno degli esperimenti svolti. In questa analisi si è voluto prima analizzare la circolazione di solido tra i due reattori del chemical looping, per poi analizzare il fuel reactor e sommare le informazioni e capire il comportamento complessivo del chemical looping con particolare attenzione per il membrane assisted chemical looping reforming.

**Parole chiave:** Reattori a letto fluidizzato circolanti, PIV/DIA, sensori di pressione, circolazione di solido, reattori a letto fluidizzato, reattori a letto fluidizzato con membrana e membrane assisted chemical looping reforming.
Chapter 1

Energy situation and novel reactors

1.1 Energy Situation in the world

In the last few years, modern society has started to deal with some changes related to the energy market of the world, change in fossil fuels market, increase of energy demand, global warming and climate change.

Within the scientific international community it is now generally accepted that human activities are responsible for recent climate changes; in particular it is believed that the increasing of greenhouse gas emissions as CO₂ has the highest impact on the actual global warming. The awareness of the connection between human activities and climate changes forced the international community to think about an environmentally sustainable development. The reduction of greenhouse gas emissions is one of the most important challenges for modern society and this came into reality in 1997 through the Kyoto protocol. The countries that decided to ratify it (countries Annex I) had to reduce between 2008 and 2012 greenhouse gas emissions in 5.3% compared to the values in 1990. The Protocol started in 2005, after it was ratified by a number of countries responsible of more than 55% of global emissions, where it was established for every nation a specific target of greenhouse gas emissions to respect. At that time, the main polluters were USA, Europe and Russia.

Fifty-five countries expect for USA and China submitted the Kyoto protocol. The developed countries were not involved in the protocol, even if some countries took the initiative to reduce their emissions. In fact, the Europe Union decided to decrease the emissions of 8% compared to 1990. The main objective of these documents was to stabilize greenhouse gas emissions to the atmosphere in a short-term period. Within this protocol, several greenhouse gases were considered as responsible of climate change: CO₂, N₂O, CH₄, SF₆, HFCs and PFCs.

In order to respect the objectives of Kyoto protocol, countries had two options: national and international approach. The internal measures consist in:

- improving power plants efficiency to reduce fuel consumptions;
- developing cogeneration plants;
- varying fossil fuels mixture giving priority to natural gas due to its lower carbon content;
- using more renewable energies, biofuels and hydrogen as energy carrier;
- increasing nuclear energy production;
- integrating power plants with systems for CO₂ capture (CCS).

External measures are flexible mechanisms as the Joint Implementation and the Clean Development Mechanism that allow countries included in Annex I to develop projects to reduce CO₂ emissions in foreign countries and to use credits from these projects to reduce their own emissions. These mechanisms are very important because they give flexibility to the countries in order they can choose the best strategy to minimize their abatement costs.

The United Nations framework convention on climate change and Kyoto protocol predict that the reduction in emissions could be obtained with the minimum possible cost. However, countries in Annex I have a different economic and energy structure, with different abatement costs. The most costs were supported from countries during that time, had a production structure less efficient based on an intensive use of carbon, like Germany, England or Luxembourg while for countries had a good energy efficiency in industrial sector,
as Italy, was given a reduction emission objective that due more expensive marginal costs. In fact for the countries with a low ratio between energy consumption and gross domestic product, it results more difficult and expensive to reduce further the necessary quantity of energy in order to produce a unit of output compared to the countries with a high ratio between energy consumption and gross domestic product.

Moreover Kyoto protocol considers three relevant subjects that should be studied at international and national level: the vulnerability of population due to the impact of climate changes, above all for developed countries, policy operations in order to promote the adjustment of economic and energy system to the climate change and interventions to reduce the climate changes. According to the report on climate change in 2013 by the Intergovernmental Panel on Climate Change (IPCC), the temperature on the surface has continuously increased since the 19th century (after industrial revolution), while the three past decades have been successively warmer and the decade of 2000 century has been the warmest ever reported.

In the last years, many efforts have been taken to reduce CO₂ emissions. In fact, during the Paris meeting on December 2015 [3] the most important key points reached as agreement are:

• To peak greenhouse gas emissions as soon as possible and achieve a balance between sources and sinks of greenhouse gases of the second half of this century
• To keep global temperature increase “well below” 2 °C and put efforts to limit it to 1.5 °C.
• To review progress every five years
• 100 billion $ a year in climate finance for developing countries by 2020, with a commitment to further finance in the future.

![Carbon dioxide emissions](image)

**Figure 1.1 CO2 emissions in the years**

Even if most of the countries ratified the protocol and decrease their own emissions, the total emissions in the world did not decrease from 1998 until 2014, as it is possible to see in the figure 1.1, because a lot of developing countries, as China and India increased their population and their primary energy consumption in a significant quantity. At the end of 1998 the country with the higher emissions was Unites States, but in 2014 China overpassed it, as it is possible to see in the figure 1.2
The trend of primary energy supply in the world is increasing during the last years and it will grow by 90% in non-OECD countries while in OECD countries, the increase is only 17%. The emissions in Gt from development countries as China, India, Africa and Latin America became considerable in the last years. It means that developing countries have started to consume more energy than before without taking care of the environment.

In the first time of its development, as it happened in Europe from 1870 with the second industrial revolution or in China from 1980 when the intensive use of coal started, a country is more interested in its economic and energy growth than global sustainability. According to the international agency of energy, by 2035 the energy demand will grow to 65% in Asia, especially in China and India, 8% in Africa and 8% in Latin America, which means that the energy market is expanding due to new developing countries. China is the main driver of increasing energy demand in the current decade, but India will take it over in 2020 as the principal source of growth. This consideration means that there are new countries involved in the energy market and that emissions cannot be decreased if first the developed countries do not pay attention to the environment. As it is possible to see in figure 1.3, within 2035 the primary energy demand in the world will reach huge values because of the new actors that are going to enter in the energy market, such as Africa, South Americana, and the countries that are developing now, like China and India.
Even if many countries are moving towards alternative and renewable energies, fossil fuels, which include oil, natural gas, and coal, are still the primary energy source for electricity, transportation, and residential services. Fossil fuels consumption has increased during the last years and according to statistic predictions, it will keep increasing until 2040. The increase in natural gas consumption is related to the increased supply of tight gas, shale gas, and coal bed methane. The use of coal is assumed to grow faster than petroleum and other liquid fuels till 2030, primarily because of its growing demand in the developing countries. Fossil fuels are attractive because of their relatively low cost compared to renewable sources such as biomass, wind, geothermal and solar power. Since new actors that belong to developing counties are taking part into the energy consumption, sometimes without any attention for the environment, it becomes necessary to move from fossil fuels to alternative fuels.

Figure 1.4 Fuel mix in 1973 and in 2012

From 1973 to 2012, even if the environmental attention was increased, the percentage of coal and natural gas respect to the total consumption has increase, as it is possible to see in the figure 1.4, while the use of oil has decreased probably because of oil crisis. As depicted in the figure 1.5, the energy consumption in the
world is continuously increasing, even if the requests especially for Europe, Eurasia and North America have decreased compared to the last five years.

Coal is the most pollutant fossil fuel compared to oil and natural gas due to its lower heat of combustion, which requires the use of more coal for the same amount of energy.

The usage of renewable sources is increasing in an exponential trend over the last years aiming at achieving the maturity of the technology. It happens to all possible renewable sources except for hydroelectricity, which is more or less constant because especially in Europe the main gaps available are all saturated.

1.2 Energy policies

According to energy policies, CO₂ concentration in the atmosphere has increased from about 280 ppm in pre-industrial period till 390 ppm in 2010, in order to avoid the increase of temperature, CO₂ concentration should not increase above 450 ppm in atmosphere. Only following the scenario of 450 ppm for the 21st century, it is possible to obtain this purpose, but this implies a decrease in the use of coal and oil for giving space to renewable and nuclear energies as is showed in pictures 1.6 and 1.7.

The three different possible scenarios regarding energy policies as summarized below:

1. **Current policies scenario**
   In this scenario no new policies are assumed to be implemented and therefore only those policies that have been adopted until middle 2011 are in force.

2. **New policies scenario**
   In this scenario it is assumed, that policies and plans to tackle climate change, energy insecurity and environmental pollution which have been announced by countries are set into force. This includes renewable energy and energy efficiency targets and support, plans for phase-out of nuclear energy and other national agreements for greenhouse-gas emission reductions. For countries where uncertainty over climate policy is very high, the scenarios assume that the policies adopted are not able to reach their target. In this scenario, the use of coal, natural gas and oil is expected again.

3. **Scenario 450**
   The 450 Scenario assumes measures in the energy system that are able to meet the global objective of limiting the global temperature rise to 2°C (in comparison to the pre-industrial levels) with a chance of 50%. For the achievement of this goal a long-term stabilization of CO₂-equivalent concentrations of 450 ppm in the atmosphere is necessary. Therefore the scenario assumes an ambitious policy action until 2020 and afterwards economy-wide emissions targets for 2035 and beyond for OECD countries and other important economic power. In this scenario, the consumption of coal and oil is not still allowed if it wants to avoid the reach of 450 ppm of CO₂ in the atmosphere. It is expected an intensive use of renewables energies and nuclear plants.

![Picture 1.6 Future trend for world TPES](image)
Investment in the 450 Scenario is only a little higher than other scenarios, but it is oriented more strongly towards low-carbon energy supply and energy efficiency.

1.3 Issues related to fossil fuels

The fossil resources are mainly used as fuels for heat production, for non energy-uses (oil), or in the petrochemical industry as raw materials for the production of various substances. Although the undoubted practical and economical advantages of fossil fuels as energy source, its massive use leads to a number of serious disadvantages, which have only been seriously considered by the society in the last years due to the observed impact on the climate change. Those disadvantages can be summarized as follows:

1. One of the main important problems related to fossil fuels is the scarcity of this resource, which is a technical limit that is not possible to overcome. Sooner or later, fossil fuels will finish and new energy sources should take over the energy demand.

2. The second problem is related to a socio-political question: fossil fuels are not evenly distributed on the earth’s surface, thus the countries that do not possess them are strongly linked to the countries with resources in abundance.

3. The most important issue is an environmental concern related to the fact that the sources are exploited by combustion reactions for most of the uses. The burning of fossil fuels causes the release into the atmosphere of pollutants such as carbon monoxide (CO), oxides of nitrogen and sulfur (SOx and NOx), unburned volatile organic compounds (VOCs), and particulate matter particulates (PST), but mainly carbon dioxide (CO2) in the amount and mode variable depending on the specific fuel and the conditions in which it occurs combustion.

The carbon dioxide together with other gases such as methane (CH₄), nitrous oxide (N₂O) and water vapor, is the primarily responsible for the greenhouse effect, a natural phenomenon that occurs in other planets of the solar system due to different transparency of the atmosphere with respect to the different frequencies of electromagnetic waves. The excess of carbon dioxide alters the balance making the atmosphere more opaque to infrared light output; in this way it is maintained on the
planet a greater amount of heat with the resulting rise in global average temperature and the alteration of the regime global climate.

The CO₂ released by burning fossil fuels is actually the same that plants and other organism prehistoric stared in organic subtracting atmosphere hundreds of millions of years ago. It is still fed back in the natural cycle of the normal decomposition or combustion of organisms, but its re-introduction into the atmosphere in times that of scale geological can be considered very short abruptly alter the natural balance.

4. Another important question is related to the variable costs of fossil fuels especially of oil because of power games from countries which own the fuels as observed in Figure 1.8.

![Figure 1.8 Crude oil prices 1861-2014](image)

1.4 The ways to reduce CO₂ emissions:

For a generic energy system, the efficiency is defined as the ratio between the energy consumption and the primary energy supply, as it is possible to see in the figure 1.9. If we look at the world, the primary energy supply is 13371 Mtoe, while the total world energy consumption is equal to 8979 Mtoe. The efficiency mean of the industrial processes for energy conversion is around 50%, and the energy losses are really high in the energy conversion.

![Figure 1.9 Energy efficiency and losses](image)
There are several options available to decrease global CO₂ emissions. In order to identify them, it is helpful to consider the most important factors influencing CO₂ emissions and relate them to energy consumption. This can be done with the simple but useful Kaya identity in the equation (1)

\[ F = P \times \left( \frac{G}{P} \right) \times \left( \frac{E}{G} \right) \times \left( \frac{F}{E} \right) \]  

(1)

Where \( F \) represent global CO₂ emissions from human sources, \( P \) is the global population, \( G \) is the gross domestic product, \( E \) is the global primary energy consumption, \( \left( \frac{G}{P} \right) \) is the global per-capita gross domestic product, \( \left( \frac{E}{G} \right) \) is the global energy intensity and \( \left( \frac{F}{E} \right) \) is the global carbon intensity of energy.

Most scenarios predicting the future development of the world suggests that the world population \( P \), and the global per-capita gross domestic product \( \left( \frac{G}{P} \right) \) will continue to increase in the near future. Therefore it can be said that the Kaya identity implies that achieving deep reduction in CO₂ emissions will require either major reduction of global energy intensity, or a steep reduction of carbon emissions from energy technologies. The most frequently options to reduce CO₂ emissions are summarized after:

- **Reduce global energy intensity**
  
  This could be achieved either by more efficient energy use in production and consumption of goods and services, or by a change in consumption patterns away from particularly energy-demanding products. In order to reduce, the environmental impact it is possible to reduce the total energy consumption in the world, but it depends on the habits of people and it need an education to understand how it is important not to waste energy. The second possibility is to reduce the energy losses but it is possible only by increasing the energy efficiency of processes. Reducing global energy intensity should be a technically sound and economically rational way to start limiting global CO₂ emissions, but it is not likely that it would be enough to mitigate global warming.

- **Increase the use of renewable energy sources**
  
  Renewable energy sources produce no direct CO₂ emissions, so an increase in its use would reduce the \( \left( \frac{E}{F} \right) \) factor in the expression (1). Unfortunately replacing fossil fuels with renewable energy is a gigantic task. Most rivers suitable for hydro power are already developed. Wind power and solar power are promising and have large potential, but still in its maturity period until they might become major players on the global energy market. Production of various kinds of biofuels is technically possible, but limited by lack of fertile land and fresh water resources. There are also concerns that large-scale use of biofuels would compete with food production, which could increase the problems with food scarcity in poor countries.

- **Increase the use of nuclear power**
  
  Nuclear power produces no direct CO₂ emissions, so increased use would reduce the \( \left( \frac{F}{E} \right) \) factor in expression (1). Very few nuclear power plants have been constructed over the last 25 years though. The private sector, which dominates the power sector in most developed countries nowadays, has shown only modest interest in nuclear power. This can likely be contributed to high investment costs and complex juridical setting. In addition to this, nuclear power also involves political considerations such as the risk for weapon proliferation, the problematic waste disposal and a lack of public acceptance in many countries. It shall also be noted that nuclear power is not a renewable energy source, and that deposits of uranium suitable for extraction with present technology are limited. However, uranium is fairly abundant and exists in very low concentrations both in the oceans and in the earth’s crust. Therefore it seems reasonable to believe that improved extraction methods and higher price would increase the commercially viable deposits considerably.
• **Switch to less carbon intensive fuels**
If coal is replaced by oil or natural gas, the emission of CO₂ per unit energy produced decreases. This is because coal contains more carbon per unit of energy than oil and natural gas. Hence fuel switch away from coal to other fuels could be used to reduce CO₂ emissions by reducing the \((F/E)\) factor in expression (1). This concept has two obvious shortcomings. Firstly, oil and natural gas are fossil fuels that emit CO₂ to the atmosphere when utilized. Secondly, the known deposits of oil and natural gas are limited and strained, while there are immense amounts of coal available at relatively low cost. So in medium or long term, fuel switch from coal to fossil fuels with less carbon intensity does not seem like a viable strategy.

• **Enhance CO₂ uptake in biomass**
Growing plants consume atmospheric CO₂ through photosynthesis. The CO₂ is converted to various carbon containing compounds building up biomass. So if the total amount of biomass on the earth were increased, considerable amounts of CO₂ could be drained from the atmosphere. This could be achieved for example by growing forests in deserts and arid lands. At present, the opposite is happening. In many parts of the world old forests are cut down for wood and farmland. Such large-scale deforestation contributes to increased CO₂ concentration in the atmosphere instead.

• **CO₂ capture and storage**
This thesis deals with technologies that can be used for CO₂ capture and storage, a way to reduce the \((F/E)\) factor.

### 1.5 Hydrogen as an alternative fuel:

A possible middle term solution to the problem of CO₂ emissions more than the carbon capture and storage is to use hydrogen as energy carrier: since it has no carbon content, hydrogen can be used as an alternative fuel without CO₂ emissions.

Molecular hydrogen is a clean fuel inherently clean because being completely free of carbon, it can be burned without producing CO, CO₂, particulates and other carbonaceous residues. Therefore, only if produced from renewable sources, hydrogen can be considered as completely clean fuel. An ideal alternative fuel should be inexpensive, convenient to use, clean, and with lower carbon content. Among various alternatives, hydrogen fuel offers the highest potential benefits and possesses most of the key criteria for an ideal fuel and is a potentially emissions-free alternative fuel with a very high specific energy content of about 140.4 MJ/kg.

The huge interest for hydrogen production and utilization is based on the premise that the fuel cell is a proven technology and hydrogen is abundant on the Earth. However, hydrogen on the Earth is in its oxidized state, \(\text{H}_2\text{O}\), which has no fuel value, and there are no other natural resources for hydrogen. Fortunately, hydrogen can be produced using both renewable and non-renewable resources. The available technologies for hydrogen production are the reforming of natural gas, gasification of coal and biomass, and the splitting of water by water electrolysis, photo-electrolysis, photobiological production, water-splitting thermochemical cycle, and high temperature decomposition.
Processes are classified depending on the reactants: oxidant and hydrocarbon charge. It refers to steam reforming when endothermic conversion of hydrocarbon with \( H_2O \) is the main reaction; to partial oxidation when exothermic reaction with \( O_2 \) are the main ones; to autothermal reforming when \( O_2 \) and \( H_2O \) are co-fed so to thermally balance the conversion process. We refer to gasification when a solid fuel, coal, biomasses, heavy refinery residuals, is transformed into syngas (\( H_2/CO \) mixture).

The importance of hydrogen as fuel is related to several factors:

- The minimal environmental impact because hydrogen is an energy vector converted from water
- Hydrogen is a non-polluting fuel for transportation vehicles and power production
- Hydrogen can be produced from fossil fuels with \( CO_2 \) capture and storage or from renewables

### 1.6 Hydrogen production processes

#### 1.6.1 Conventional steam methane reforming

Currently, SMR is the most common and the least expensive industrial technology to produce hydrogen. Methane reacts at a high temperature 700–1100 °C with steam to form syngas [4].

\[
CH_4 + H_2O \rightarrow CO + 3H_2 \quad (1)
\]

\[
CO + H_2O \rightarrow CO_2 + H_2 \quad (2)
\]

\[
keq(T) = \frac{P_{CO} * (P_{H_2})^3}{P_{CH_4} * P_{H_2O}} = \frac{x_{CO} * x_{H_2}^3}{x_{CH_4} * x_{H_2O}} * p^2 \quad (3)
\]

The reaction (1) is the steam methane reforming, while (2) is the water gas shift that has the purpose to convert \( CO \) in \( CO_2 \), in order to avoid the problem of toxicity related to \( CO \). Both reactions are equilibrium limited and it is impossible to achieve complete conversion of \( CH_4 \) and \( CO \) in a single reactor under normal reaction conditions. At the equilibrium the constant of reaction is described by equation (3) and it shows that for high pressure the concentration of products has to decrease to keep the value of \( keq \) constant.
Figure 1.11 Methane conversion for different temperature conditions

The steam methane reforming reaction is supported at higher temperature because it is an endothermic reaction. At atmospheric pressure and with a $H_2O/CH_4$ ratio equal to 1, the complete conversion of methane is reached at 900 °C.

The situation is different when the pressure is increased because the process is characterized by an increasing number of mole. The problem is that operate with a high pressure is necessary in order to limit the machinery volume and because most of applications need pressurized hydrogen. The reaction (2) of water gas shift starts when there is $CO$. There is a strong dependency on the pressure as it is possible to see looking at the kinetic constant and when the system is pressurized, it is not possible to reach the total conversion at 900 °C but only with a temperature of 1400 °C.

Figure 1.12 Conversion of methane depending on temperature and pressure

With a high pressure it is not possible to obtain the total conversion of methane because the temperature could not reach 900 °C for reasons connected with the resistance of the materials. In order to obtain a good conversion it works with a $H_2O/CH_4$ ratio equal to 2.5-4.5. The use of a great excess of $H_2O$ help to avoid the accumulation of black smoke supporting the reaction

$$ C + H_2O \rightarrow CO + H_2 $$

(4)
Since the methane is the important reactant of the process, it is possible to change the operative conditions to improve the conversion, viz. changing the $H_2O/CH_4$ ratio. If this ratio is increased, it is possible to obtain higher methane conversion at lower temperature. It makes constant the product of molar fraction feeding more water in order to improve the conversion of the methane.

Figure 1.11 shows that the composition is shifted towards the products at high temperature and low pressure; by the way for technical reasons it is better to operate at high pressure to reduce equipment volume and because in this way $H_2$ is already available at high pressure as all the industrial applications required. For this reason most of processes generally work at temperature around 850-900°C and pressure 25-30 bar.

For the kinetic of reaction, in order to operate in good condition according to the thermodynamics, the process requires a catalyst. The use of a catalyst solves a lot of problems but introduce the problem of the carbon presence. The preferred one is Ni, generally spread on a support to increase the surface of contact and to control temperature values.

The reaction (4) is important, not because it is able to produce hydrogen but because it helps to keep the catalyst without carbon. The catalyst is arranged in tubes with a diameter of 7-13 cm that need to be reduced in order to obtain an efficient heat transfer. In the last years, steam reforming was used to convert a fuel in a suitable gas for fuel cell. In this case the choice of fuel is related to the kind of fuel cell in which are interested.

Steam reforming converts hydrocarbon in hydrogen and carbon oxides. This reaction expands the gas and it needs conditions of low pressure and high temperature to happen in an efficient way. The thermodynamic reversibility of steam reforming and partial oxidation reactions limits the maximum $H_2$ product yield and $CH_4$ conversion, which in conventional large scale processes necessitates purification of $H_2$ using high and low temperature shift reactors, $CO_2$ separation steps, preferential CO oxidation units, and pressure swing absorption units.

In industrial application for large scale, the most efficient technology is not based only on the steam reforming. The economies of scale feasible for industrial steam reforming unit are smaller than the processes based on partial oxidation and air separation. As a solution to overcome the thermodynamic limitations, reactor operation with an integrated product separation can be devised using permselective membranes that shift the reaction equilibriums in favorable direction and facilitate removal of the reaction product. The final step in steam methane reforming is the separation of the hydrogen from syngas exiting the water gas shift reactor. The three most common methods are:

- Pressure swing adsorption to separate hydrogen
- Adsorption of $CO_2$ in MDEA columns followed by condensation of the remaining H2O
- Membranes to separate the hydrogen

### 1.6.2. Partial oxidation

In steam reforming, heat has to be supplied externally by burning part of the fuel. To overcome this problem, it heat essential for endothermic reactions can be supplied inside the reactor itself through the development of exothermic reactions.

This is the technology referred to as partial oxidation. Currently, this process is carried out in the absence of catalyst by feeding methane and oxygen in suitable amounts within a reactor constructed in order to operate
under adiabatic conditions. In the first part of the reactor, the oxidative processes take place in order to generate heat and steam for the subsequent course of the reforming reactions, which they will be conducted in the second part of the reactor until the thermodynamic equilibrium is reached. The key parameter in partial oxidation is the ratio between $O_2/CH_4$, which leads into the reaction depicted in equation 6.

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$$

A value of $O_2/CH_4$ equal to 0.5 is normally used. On one hand it supports the development of products obtained through the partial oxidation compared to total combustion. On the other hand, it avoids the reaching of high temperatures in an autothermal way. The remaining methane will be inclined to pyrolysis and not to steam reforming, which produces black smoke and implies a low value of conversion. To let system reaches the high temperature, it will be necessary to operate with a ratio between $O_2/CH_4$ higher than 0.5 in order to take place the total combustion. It means that there will be a reduction of selectivity but the system is able to operate at high temperature in an autothermal way. With the partial oxidation, the problem of endothermic process is solved, nevertheless this process is used only for heavy hydrocarbons because the costs related to a system of air separation, coke deposition and the difficult control of a reaction that could become unstable, and giving as results CO$_2$ and water, it make the partial oxidation affordable only when the conventional steam reforming could not be used.

![Figure 1.13 Partial oxidation system](image)

**1.6.3 Autothermal reforming**

Autothermal reforming is a favorable process, which combines the effects of both the endothermic steam reforming and the exothermic partial oxidation. The feed consists on $H_2O, O_2$ and $CH_4$ in such ratios as to ensure that the system will be self-sustaining without development of black smoke. In this system the heat essential for reforming is supplied by methane oxidation reaction. The charge of natural gas and $H_2O$ is fed in a reactor with sub-stoichiometric oxygen amount to have partial combustion in order to produce the heat required for the reaction. The reactor is divided in two sections: a combustion chamber where the oxidation of natural gas takes place, and a reforming chamber full of catalyst where the steam reforming reaction can occur thanks to the heat spread by the combustion. To avoid that the catalyst reaches too high temperatures, the reforming section is divided from the combustion chamber with a radiation shield. It is also necessary to insert a refractory layer to keep the metallic wall below maximum resistance value.
Many authors have verified that add water in the mixture of partial oxidation imply an increase of hydrogen produced and a reduction in the temperature of the catalytic reactor. This translates, for a given moles of hydrogen to produce, in a greater compactness of reactor and in lower thermal deactivation of the catalyst compared to the process of partial oxidation. For these reasons, the addition of water to the mixture of partial oxidation makes the process possible within the decentralized production of hydrogen. In this configuration the steam to carbon ratio is between 1 and 2 because the presence of oxygen decreases the risk of carbon formation and deposition. Common values of $O_2/CH_4$ ratio are 0.55-0.6. The oxidant introduced in the reactor can be pure oxygen or air. To produce pure $O_2$ it is necessary an ASU which is a very expensive component; on the other hand the use of air implies a big amount of inert $N_2$ that has to be heated up to 1100 °C without taking part in the reaction. This involves a loss of energy efficiency and bigger volumes, especially for PSA unit, with higher costs. For this reason the best solution should be the one with ASU. Thus it is possible to have an ATR+HESR (Heat Exchange Steam Reforming) configuration, where the syngas out of the reactor provides the heat for warming up and pre-reforming the feedstock charge. To avoid metal dusting problems particular heat exchangers have to be used.

1.7 Why moving towards novel reactors and motivation of this work

In a world in which the main fuel used are fossil, it could be interesting to move towards alternative fuels like hydrogen, in order to avoid the problem related to variable fossil fuel costs, dependence on the other countries and damaging emissions.

Novel reactors are being studying in order to produce pure and clean hydrogen. The main are:

- Fluidized bed reactors
- Fluidized bed membrane reactors
- Chemical looping reactors

The advantage of these reactors is the production of hydrogen as an alternative fuel that can be used in the fuel cells avoiding the mechanical conversion for electricity production. The most important issue related to chemical looping reactors is the possibility to obtain pure hydrogen, with CO$_2$ capture and in an autothermical way, avoiding the high external demand required in the traditional steam methane reforming reactors. These concepts are studied in detail in chapter 2.
Chapter 2

Novel reactor concepts for energy production

2.1 Fluidized bed Reactors

In fluidization an initially stationary bed of solid particles is brought to a fluidized state by an upward stream of gas or liquid as soon as the volume of the fluid exceeds a certain limiting minimum fluidization velocity.

In fluidized beds the particles are suspended by the fluid stream and at such conditions the pressure drop of the fluid passing through the fluidized bed is equal to the weight of the solids minus the buoyancy, divided by the cross-sectional area of fluidized bed reactor, according to the equation (2)

\[ \Delta p_{f_b} = \frac{A_t \star H \star (1 - \varepsilon) \star (\rho_s - \rho_g) \star g}{A_t} \]  

(2)

Where the porosity \( \varepsilon \) of the fluidized bed is the void volume of the fluidized bed divided by the total bed volume, that is the volume in interstice between grains but not including any pore volume in the interior of the particles; \( \rho_s \) is the solids apparent density and \( H \) is the height of the fluidized bed.

As the volume flow rate or the superficial gas velocity of the fluid increases beyond the value of minimum fluidization velocity as it is possible to see in figure 2.1a, one of two things happens:

- in fluidization with a liquid, the bed begins to expand uniformly;
- in fluidization with a gas, solids-free gas bubbles begin to form, as it is possible to see in figure 2.1b.

The local mean bubble size increases rapidly with increasing height above the grid because of coalescence of the bubbles. If the bed vessel is sufficiently narrow and high, the bubbles fill the entire cross section and pass through the bed as a series of gas slugs, as it is possible to see in figure 2.1c. As the gas velocity increases again, more and more solids are carried out of the bed and the solids concentration decreases continuously with increasing height. To achieve steady-state operation of such a “turbulent” fluidized bed, shown in picture 2.1d, solids entrained in the fluidizing gas must be collected and returned to the bed. The simplest way to do that is with a cyclone integrated into the bed vessel and a standpipe dipping into the bed. A further increase in gas velocity leads to the circulating fluidized bed, shown in picture 5e, which is characterized by a much lower average solids concentration than the previous system.
Circulating fluidized bed reactors are characterized for a fast fluidization with a great solids transport. In order to obtain a fast fluidization, it is essential to have high superficial gas velocity and low particle diameter compared to the bubbling fluidized bed reactor. The velocity profile of the solids is not uniform but depend on the gas stream. Near the wall the friction reduces the velocity of the gas that is not able to support particles moving downwards. The superficial gas velocity is higher in the center of the bed and the main characteristics of circulating beds are:

- High solid mixing
- Good gas-solid mixing due to the high gas velocity and higher compared to the bubbling bed for the lack of by-pass due to the bubbles

The motion of the gas is similar to a plug-flow, which also helps the conversion of the gas phase.

### 2.1.1 History and industrial application of fluidized bed

The first fluidized bed reactor for industrial applications was developed in order to gasify coal by the German engineer Fritz Winkler in the early 1920’s. Winkler patented this gasification technology in 1922 and the first large scale industrial unit was built in Leuna, Germany in 1926. Little advancement in the technology took place between the Winkler patent and 1942 when the Fluidized Catalytic Cracking process of kerosene by the Standard Oil Company was developed. The Standard Oil Company built the first industrial FCC unit in Baton Rouge, Louisiana, for this process. Their improvement led to a great interest in fluidized bed reactors because of their ability to convert large amounts of petroleum into usable energy efficiently and relatively clean. The study of these reactors soon blossomed, first concentrating on the fluidization characteristics of the fine particles used in the FCC process, then moving on to more coarse materials. Afterwards appeared the roasting of sulfide ore in 1947, the drying of dolomite particles in 1948 and the introduction of the Fischer-Tropsch plant in the 1950’s for the conversion of natural gas to gasoline. The large interest in this technology soon demanded a deeper understanding of the mechanics and hydrodynamics of the reactors for modelling purposes. Toomey and Johnstone in 1952 proposed the first generalization, defining the minimum fluidization velocity, stating that all excess gas in the bed acts much like bubbles in a column of water. They noticed that the mixing of the bed material was due to an entrainment of particles in the wakes of upward moving bubbles, giving the bed excellent heat transfer properties. They also found that gas by-pass limited the gas-solid reactions in the bed because of the large amounts of gas within bubbles that were devoid of bed material. These empirical studies eventually led to the proposal of the first theory of bubble motion in 1961 by Davidson.
Fluidized bed applications can be divided into four types: 1) gas catalytic reactions, 2) gas-phase reactions, 3) gas-solid reactions, and 4) physical processes. The first type describes a reaction taking place on a catalyst surface with the continuous phase, such as the Fischer-Tropsch process. The second type uses a solid, such as refractory sand, to supply heat for a reaction or to transport heat out of the system. An example would be the thermal cracking process. The third type is a reaction where both gas and solids are the reactants. Gasification is an example of this reaction type. The fourth type does not have a reaction that occurs but describes a physical process, for example, particle drying. The reactants and products from the first and second reaction types are both contained in the continuous phase. In the third reaction type the reactants are both solid and gaseous while the products contain either 1) only a gas phase or 2) a combination of both gas and solids, such as ash.

### 2.1.2 Fluidization Regimes

Fluidization behavior may differ based on the operating conditions of the reactor such as gas velocity and gas and solid properties. Upon these observations, researchers have long established the existence of different fluidization regimes which are illustrated in figure 2.2. The state of fluidization begins at the minimum fluidization velocity $u_{mf}$. As the gas flow across the bed is increased, there exists a velocity known as the minimum fluidization velocity, $u_{mf}$, at which the resulting pressure drop is high enough to lift and suspend the solids by balancing the weight of the bed.

![Fluidization regimes](image)

**Figure 2.2 Fluidization regimes**

When the gas flow is further increased, the bubbling regime is reached. This regime starts when a minimum bubbling velocity, $u_{mb}$, is reached, where bubbles appear and a distinction between the bubble and emulsion phase can be established. As these bubbles move upward in the bed, they tend to burst at the bed surface ejecting particles into the freeboard. Due to the mixing in the bubbling bed, the solids phase behaves as a continuous stirred tank reactor, while the hydrodynamic of the gas phase is more complex, with a behavior close to plug flow. The mixing leads to a great heat transfer with uniform temperature and a gas-solid contact quite good.
Chapter 2

The bed at incipient fluidization conditions consists of an emulsion of solids inside the gas stream with homogeneous characteristics in all the volume of the bed. For particles in Geldart B and D, as soon as the fluidization velocity exceeds the $u_{mf}$ value, bubbles start to form. They are cavities filled with gas and in most of them, the presence of solid phase is limited or even absent. Since the density of the bubble is lower compared to the emulsion phase, the bubbles pass through the bed because of the buoyancy forces. The size of the bubble increases while it reaches the top of the bed because the pressure inside the emulsion phase decreases. The linear pressure variation in the bed lead to the fact that when the bubble going up to the reactor, a stream of gas enters in the bottom part of the bubble and go out from the top part. The mass transfer between the gas in the bubble and the gas in the interstitial phase that is slower involves a great mixing in the system and helps the reactions and heat and mass transfer between the gas and the solids. The size of a bubble grows with the increase of the particle diameter and the velocity of the gas because the velocity in the interstitial phase is almost constant, while the gas excess passes through the bubble and help it to grow. The bubbles can grow until a certain dimension, after it they will explode. It causes solids jets on the dense phase of the bed. The concentration of the solids in a fluidized bed assumes an axial distribution as it is possible to see in the figure 2.3.

![Figure 2.3 Schematic drawing of boiling fluidized bed and freeboard](image)

Most of the solids are located in the dense phase in the bottom part of the reactor, above it the solids concentration decreases in the splash zone, region in which happen the return of solids characterized by the most size above the dense phase. The next zone is called disengaging zone and it is characterized by few particles that behave like isolated particles. Bigger particles, for which the terminal velocity is higher than the gas superficial velocity, fall down in the dense phase, while fine particles are carried in the higher part of the bed, called dilute zone.

When the velocity is increased, the bed expands again until it reaches a change in the fluid dynamic regime characterized by huge pressure fluctuation, this is the transition phase between the fluidized and turbulent regime of fluidized bed reactors. When the turbulent regime becomes stabilized, the pressure fluctuation decreases and the bubbles appear vague because of the fast coalescence and break. The turbulent regime is reached when the terminal velocity of the ejected particles is surpassed by the gas and the bed material no longer falls back as it is entrained out of the reactor. A solid particle collection device such as a cyclone or
filters is usually placed at a high enough height to ensure particles recirculation and avoid depletion of the bed as the velocity is increased. Under these conditions, despite bubbles often losing their shape, beds with recognizable surfaces are referred to as turbulent fluidized beds. The bed porosity increases and higher parts of the dense zone are not evident.

The fast fluidization regime is characterized by the dominance of the gas phase and the bed level disappears due to a further increase in gas velocity. The transition velocity from the turbulent to the fast fluidization regime is referred to as the transport velocity, \( u_{tr} \), with reactors operating under these conditions known as fast fluidization fluidized bed reactors. Finally the pneumatic transport is reached when all of the bed is depleted. The fast fluidization regime happens with small particles, higher superficial gas velocity and higher solids flux. The fact that the velocity is really higher compared to the terminal velocity of the particles implies a huge solids circulation rate. For this reactor, the axial solids distribution is quite different because it lacks of the splash zone and the solids presence decreases with continuity following an exponential equation from the dense to dilute zone with the trend in the picture 2.3.

Depending on the desired product or the wanted effect, fluidized bed reactors can be operated in any of the afore mentioned regimes. For instance, due to many distinct advantages, turbulent fluidized bed reactors are sometimes preferred to both bubbling and fast fluidization reactors because of their dynamic gas-solids contacting, high solids holdup, high exchange rate of the gas between the void and the emulsion phases, and relative spatial uniformity in flow properties. At low gas velocities in the range of fluidization, the rising bubbles contain very few solid particles. The remainder of the bed has a much higher concentration of solids in it and is known as the emulsion phase of the fluidized bed. The bubbles are shown as the bubble phase while the cloud phase is an intermediate phase between the bubble and emulsion phases.

Figure 2.4 Schematic drawing of boiling fluidized bed and freeboard
Whereas the onset of the fluidized state can be described by the minimum fluidization velocity, the bed operating range and the gas velocity needed to create a given fluidized state can be estimated with the help of the fluidized-bed state diagram devised by Reh and it is shown in picture 2.4.

This plot shows the fluid mechanical resistance characteristics of the fixed bed, fluidized bed, and pneumatic transport. The ordinate is the quantity

\[
\frac{3}{4} \frac{u^2}{g \cdot d_p} \frac{\rho_g}{\rho_s - \rho_g}
\]

and the abscissa is the Reynolds number \( \text{Rep} \) formed with the fluidization velocity \( u \) and the particle diameter \( d_p \). The state parameter in the fluidized-bed region is the mean bed porosity. The use of the diagram is facilitated by an auxiliary grid with lines of constant \( M \) and constant Archimedes number. While the dimensionless groups plotted as ordinate and abscissa each contain both the particle diameter and the fluidization velocity, this is not the case with the parameters \( Ar \) and \( M \) defined by

\[
Ar = \frac{d_p^3 \cdot \rho_g \cdot (\rho_p - \rho_g) \cdot g}{\mu_g^2}
\]

\[
M = \frac{u^3}{g \cdot v} \frac{\rho_g}{\rho_s - \rho_g}
\]

The Reh status diagram can answer a number of practical questions. If, for example, the properties of the gas \( (\rho_f, \dot{v}) \) and the solid \( (d_p, \rho_s) \) and the fluidization velocity are given, the calculation of \( Ar \) and \( Re_p \) can give information, via the status point \( S \) in the diagram, on the average voidage \( \varepsilon \) in the fluidized bed. Taking the line \( M = \text{constant} \) through \( S \) at the intersection with the line \( \varepsilon \to 1 \) at \( S_1 \) gives information on the particle size which is just elutriated when particles with a size distribution are fluidized, and the intersection of the same line with the fixed-bed limit \( \varepsilon = 0.4 \) indicates the particle size at which fluidization will break down if agglomeration occurs. The line \( Ar = \text{const.} \) through \( S \) can be used to find the minimum fluidization velocity at \( S_3 \) or – as a measure of the upper limit of fluidization – the maximum fluidizing velocity at \( S_4 \). An important practical point is that the state diagram implies a classification scheme that relates various fluidized-bed systems to one another.
2.1.3 Behavior of fluidized bed

The fluidized bed offers the advantage of proper mixing over other contacting methods in which the bed materials are fully suspended in a fluid stream. Several factors affect the bed behavior out of which the following parameters have been described in detail:

- **Superficial gas velocity**: the velocity at which the continuous phase travels vertically through the particulate phase is important to the characteristic behavior of the bed. It is common to generalize this with the term superficial gas velocity because the velocity of the rising gas can vary throughout the bed. The superficial gas velocity, \( u_g \), is the volumetric gas flow rate through the bed divided by the bed cross-sectional area.

- **Minimum fluidization velocity**: when a fluid passes upwards through the interstices of a bed of solids without the slightest disturbance of the solids, the bed is called a fixed bed. With further increase in the velocity of fluid, the entire bed of solids is suspended and behaves as if its weight is
counterbalanced by the force of buoyancy. At this point all the particles are suspended in the fluid. This is called onset of fluidization and the velocity of fluid at which it happens is called minimum fluidization velocity, which is one of the most important parameter for the design of fluidizers. It is possible to calculate the minimum fluidization velocity according with the equation (2)

$$u_{mf} = \left(\frac{\mu g}{\rho_g * d_p}\right)\left(\sqrt{(27.2)^2 + 0.0408 * Ar} - 27.2\right)$$

$$Ar = \frac{\frac{d_p^2}{\mu_g} * \rho_g \left(\rho_p - \rho_g\right) * g}{\rho_g^2}$$

Figure 2.6 Pressure drop with the gas velocity

- **Terminal velocity** that is the velocity above which a particle can become entrained from the bed and it can be calculated according with the equation (3)

$$u_t = \left(\frac{4 * d_p * \left(\rho_s - \rho_g\right) * g}{3 * \rho_g * C_D}\right)^{\frac{1}{2}}$$

Where $C_D$ is the drag coefficient. The terminal velocity is the velocity obtained from the equilibrium between the gravity force, the buoyance force and the drag force as it is possible to see in figure 2.7

Figure 2.7 Particle terminal velocity


- **Pressure drop**: the pressure drop through a bed is another important parameter which controls the channel and slug formation and thereby mixing of the bed material with the fluidizing fluid. A low flow rates in the packed bed, the pressure drop is approximately proportional to gas velocity up to the minimum fluidization condition. With a further increase in gas velocity, the packed bed suddenly unlocks, resulting in a decreasing of pressure drop as it is shown in figure 2.6.

- **Sphericity**: is defined as the ratio between the surface of sphere and the surface of particle with the same volume. The impact of particle sphericity has been analyzed by very few authors through experimental studies. Therefore question about how particle shape can influence flow inside the reactor still exist. The authors state that sphericity has a notable influence on the drag coefficient and it will increase with lower sphericity under the same operative conditions.

With gas velocity beyond minimum fluidization, the bed expands and gas bubbles are seen to rise resulting in non-homogeneity in the bed. With the increase in gas flow, the pressure drop should remain unchanged but due to bubbling and slugging there is always a fluctuation in the pressure drop and it increase slightly. Particularly for coarse particles, the mean total pressure drop across a slugging bed may continue to increase with gas velocity higher than at the minimum fluidization condition. For fine particles, the variation of pressure drop with pressure drop is quasi-linear when they are fluidized by classical method of fluidization as they form cranks and channel. Particulate fluidization generally gives rise to a homogenous fluidization.

### 2.1.4 Effect of particle size and density

The behavior of fluidized solids have been divided into four groups by the empirical Geldart classification based on the difference in density between the fluidizing gas and the used particles, and by the mean particle size $d_p$ as illustrated on Figure 2.7.

**Geldart C Particles**: This group is characterized by cohesive or very fine particles (usually less than 20 microns). Due to their large surface area combined with low mass, inter particle forces tend to be greater than those resulting from the action of the gas which in turns renders fluidization extremely difficult. As a result, particles fail to flow in a manner that produces bubbles and the bed is unable to expand. The adhesion forces between particles are stronger than the forces that the fluid can exert on particles. Gas flow through the bed forms channels extending from the grid to the top of the bed, and the pressure drop across the bed is lower than the value of equation (2). Fluidization properties can be improved by the use of mechanical equipment such as agitators.

**Geldart A Particles**: In this group, particles are characterized as aeratable with a small mean particle size or/and low particle density. In fact, manufactured catalysts often belong to this group with particle sizes ranging from 20 to 100 microns, especially for fluidized bed catalytic cracker. As the gas velocity increases beyond the minimum fluidization point, the bed first expands uniformly until bubble formation set in at velocity equal to the minimum bubble velocity. The bubbles grow by coalescence but break up again after passing a certain size. At a considerable height above the gas distributor grid, a dynamic equilibrium is formed between bubble growth and breakup.

**Geldart B Particles**: These particles have moderate particle sizes and densities. Typical representatives of this group are sands with mean particle diameters between 0,06 and 0,5 mm. Due to the non cohesiveness of these particles, bubbles appear as soon as fluidization starts shifting the bed’s behavior to the bubbling regime. Bubble formation begins immediately above the minimum fluidization point. The bubbles grow by coalescence and growth is not limited by bubble splitting.
Geldart D Particles: This group includes solids with large particle diameters or high bulk densities; examples are sands with average particle diameters higher than 0.5 mm. Bubbles begin to form just above the minimum fluidization point, but the character of bubble flow is different from that in group B because Geldart D particles are characterized by the formation of “slow” bubbles.

![Figure 2.7 Geldart classification](image)

The size distribution of the particulate phase is very important for the fluidized bed hydrodynamics. If there is a large size distribution, the smaller particles will fall into the spaces between larger particles and become fluidized in these spaces before the larger particles do. This phenomenon gives an intermediate fluidization point which may be much lower in terms of gas superficial velocity \( u_g \) than \( u_{mf} \) when the bed is fully fluidized. In fact, it has been suggested that when analyzing \( u_{mf} \) for wide size distributions, a range of \( u_g \) is more appropriate than a single point.

2.1.5 Advantage of fluidized bed reactor compared to fixed bed

Fluidized beds have certain properties that give rise to various advantages over other processing systems. The smooth, liquid-like flow of particles allows continuous automatically controlled operations with easy handling. The rapid mixing of solids leads to close to isothermal conditions throughout the bed; hence the operation can be controlled simply and reliably. The well-mixed solids represents a large thermal flywheel that resists rapid temperature changes, responds slowly to abrupt changes in operating conditions, and gives a large margin of safety in avoiding temperature runaways for highly exothermic reactions. The circulation of solids between two fluidized beds makes it possible to remove the vast quantities of heat produced in large beds. A fluidized bed is suitable for large-scale operations. Heat and mass transfer rates between gas and particles are high when compared with other modes of contacting. The rate of heat transfer between a fluidized bed and an immersed object is high; hence heat exchangers within fluidized beds require relatively small surface areas.
Fluidized beds also retain some disadvantages. For bubbling beds of fine particles, the difficult-to-describe flow of gas, with its large deviations from plug flow, represents inefficient contacting. This becomes especially serious when high conversion of gaseous reactant or high selectivity of a reaction intermediate is required. The rapid mixing of solids in the bed leads to non-uniform residence times of solids in the reactor and for the continuous treatment of solids; this gives a non-uniform product and poorer performance, especially at high conversion levels. For catalytic reactions, movements of porous catalyst particles, which continually capture and release reactant gas molecules, contribute to the back-mixing of gaseous reactant, thereby reducing yield and performance. Friable solids are pulverized and entrained by the gas and must be replaced and the erosion of pipes and vessels from abrasion by particles can be serious. Lastly, for non-catalytic operations at high temperature, the agglomeration and sintering of fine particles can require a lowering in temperature of operations, thereby reducing the reaction rate considerably. Another important problem is related to the particle’s attrition and erosion of the reactor.

2.2 Hydrogen membrane

The concept of a hydrogen membrane reactor is based on Le Chatelier’s principle according to which the hydrogen produced in the reactor permeates through a membrane and exits through the reaction zone. Membranes are several microns thick and generally made of Pd or Pd/Ag or other Pd-based alloys. Palladium is the most used membrane material for hydrogen permeation because it is infinitely selective to hydrogen and has shown to have high permeability. Pd is usually alloyed with metal to increase permeability and reduce the effect of hydrogen embrittlement.

The main advantages of the membrane technique compared to the traditional steam methane reforming processes are as follows:

- no limitations of chemical equilibrium for the hydrogen-producing reaction, which means the equilibrium is shifted more toward product
- higher conversion of methane can be achieved at lower temperatures,
- generation of separate H₂ and CO₂ streams
- no need of additional CO-shift converters
- more simple and compact reactor configurations
- high overall efficiency owing to the relatively low temperature resistance of the Pd-based membranes; hydrogen membrane reactors operate at temperatures of 400–600 °C, compared to 800–950 °C typical of conventional reformers.

![Figure 2.9 Simplified concept of membrane separation](image)
The flux $J_{H_2}$ through a membrane layer depends on the properties of the layer material and of the compound $H_2$, on the thickness of the membrane and on the difference of partial pressures between the two chambers of the module. The properties of materials are taken into account by means of the membrane permeability which is affected by the temperature as well. The hydrogen molecular transport in the palladium membranes occurs through a solution/diffusion mechanism, which follows six different activated steps:

- dissociation of molecular hydrogen at the gas/metal interface;
- adsorption of the atomic hydrogen on membrane surface;
- dissolution of atomic hydrogen into the palladium matrix;
- diffusion of atomic hydrogen through the membrane;
- re-combination of atomic hydrogen to form hydrogen molecules at the gas/metal interface;
- desorption of hydrogen molecules.

Depending on temperature, pressure, gas mixture composition and thickness of the membrane, each one of these steps may control hydrogen permeation through the dense film. As a result, the hydrogen permeating flux can be expressed by means of the equation (4).

$$J_{H_2} = \frac{p_{m,pd}}{t_{m,pd}} \left( p_{H_2,ret}^n - p_{H_2,perm}^n \right)$$

where $n$ (variable in the range 0.5–1) is the dependence factor of the hydrogen flux to the hydrogen partial pressure, $J_{H_2}$ the hydrogen flux permeating through the membrane, $p_m$ the hydrogen permeability, $t_{m,pd}$ the membrane thickness, $p_{H_2,ret}$ and $p_{H_2,perm}$ the hydrogen partial pressures in the retentate and permeate sides, respectively. This equation even points out the inverse proportionality to the membrane thickness. The role of the membrane thickness is very important: on one hand, a thinner membrane offers a higher permeability; on the other hand, thicker membranes are necessary in order to ensure the mechanical resistance and strength.

The most important problem associated with the use of pure palladium membranes is the hydrogen embrittlement phenomenon. When the temperature is below 300 °C and the pressure below 2.0 MPa, the $\beta$-hydride phase may nucleate from the $\alpha$-phase, resulting in severe lattice strains so that a pure palladium membrane becomes brittle after a few cycles of $\alpha \leftrightarrow \beta$ transitions. These transitions do not take place as a change of the lattice structure, but as a lattice dilatation. The $\beta$-hydride phase formation is represented as a clustering of hydrogen atoms, whose energy of attraction, being associated with the lattice, strains around the dissolved hydrogen atom. A possible solution to avoid this phenomenon is represented by the use of a Pd alloy containing another metal, such as silver. The role of silver is explained by its electron donating behaviour, being largely similar to the one of the hydrogen atom in palladium. Silver and hydrogen atoms would compete for the filling of electron holes.

### 2.3 Fluidized bed membrane reactors

The figure 2.8 shows the fluidized bed membrane reactor: it is composed of a U-shaped membrane in which air flows and partial oxidation happens when it meets the inlet gas so the heat of the reaction is supplied in this way. The presence of the $H_2$ membrane shifts the thermodynamic equilibrium of the reactions toward
the products, increasing methane conversion even if the temperature is lower than in a conventional SMR system.

Pd-based hydrogen perm-selective membranes are integrated in a bubbling fluidized bed reactor fed with methane and steam at high temperature and intermediate pressure depending on the membranes resistance. Steam methane reforming and water gas shift reactions occur in a single unit and a pure stream of H₂ can be separated, without any other additional components and in particular a downstream adsorption unit is not required.

The heat of reaction is supplied by burning part of the hydrogen produced in the U-shape membrane immersed in the bed and fed with air. In this way it is possible to have an auto-thermal reactor, so the presence of external burners is not required: for this reason the total reactor volume can be decreased. On the other hand part of the expensive Pd-based membranes are used to burn part of the H₂ produced, with an increase of investments cost. Pure hydrogen is recovered via Palladium-based membranes inserted into the fluidized bed. A virtually isothermal condition can be achieved and bed-to-membrane mass transfer limitations are largely avoided. On the other hand, bubble-to-emulsion phase mass transfer limitations and the extent of gas back-mixing could deteriorate its performance. In particular, the use of membranes inside the reactor could decrease the extent of back-mixing and can also help decreasing the bubble diameter, enhancing the bubble-to-emulsion phase mass transfer.

![Figure 2.10 FBMR configuration](image)

2.4 Chemical looping combustion

Chemical-looping is a new technology for hydrogen production, already in the research phase but with the promise that it will substitute the conventional steam methane reforming. The technology involves the use of a metal oxide as an oxygen carrier which transfers oxygen from combustion air to the fuel in order to avoid the direct contact between air and fuel. Chemical looping has been developed as an alternative way for hydrogen production with CO₂ capture, CLR can substitute the SMR reactors of the traditional processes and the outlet stream of the CLR is sent to WGS reactors and a PSA unit for pure hydrogen production.
Commonly, the term Chemical-Looping is referred to those processes transporting oxygen. Thus, the term "Chemical-Looping" has been used for cycling processes that use a solid material as oxygen-carrier containing the oxygen required for the conversion of the fuel. To close the loop, the oxygen depleted solid material must be re-oxidized before starting a new cycle.

Chemical looping combustion has emerged as an attractive option for carbon dioxide capture because CO₂ is inherently separated from the other flue gas components, N₂ and unused O₂, and thus no energy is expended for the gas separation and no gas separation equipment is required. The chemical looping system is composed of two reactors, an air and a fuel reactor. The fuel is introduced in the fuel reactor, which contains a metal oxide, MeₓOᵧ. The fuel and the metal oxide react according to the equation (1).

\[(2n + m)MeₓOᵧ + CnH₂m \rightarrow (2n + m)MeₓOᵧ₋₁ + mH₂O + nCO₂ \]  

Figure 2.11 Schematic representation of chemical looping combustion

The reduced metal oxide, MeₓOᵧ₋₁, is transferred to the air reactor where it is oxidized: according to the equation (2).

\[MeₓOᵧ₋₁ + \frac{1}{2}O₂ \rightarrow MeₓOᵧ \]  

Chemical looping combustion shows unique potential for carbon capture because gas-gas separation is inherently avoided.

The interconnected fluidized bed reactors for CLC substitute the furnace needed in the reformer reactor. The steam reformer is a tubular fixed bed reactor horizontally immersed in the fuel reactor of the CLC system. The heat needed for the steam reforming is provided by the hot oxygen carrier coming from the air reactor where the exothermic oxidation in equation (1) of the Ni oxygen carrier happens in the system with air. The reformer gas is then cooled and sent to a HT-WGS process to increase the hydrogen recovery. Finally, a PSA unit is used for hydrogen purification, where the by-products stream is fed to the fuel reactor of the CLC system. In this case, full conversion of the hydrocarbon fuel into CO₂ is achieved. The technology presents several advantages with respect to traditional systems: auto-thermal operation is achieved in the SMR-CLC.
system, hydrogen is also separated at high pressure in the PSA, where the off-gas is employed as a fuel for the fuel reactor of the CLC, the gas product from the fuel reactor is mainly a mixture of CO₂ and steam, so after steam condensation, a high purity CO₂ stream is obtained suitable for CO₂ capture.

The air reactor is a high velocity fluidized bed where the oxygen carrier particles are transported to the fuel reactor using a cyclone. The fuel reactor is a bubbling fluidized bed reactor, from which the reduced oxygen carriers are going back to the air reactor by means of an overflow pipe.

Two important design criteria are related of the oxygen carrier:

1. The amount of oxygen carrier necessary in two reactors, the bed masses is inversely proportional to the rate of conversion of the oxygen carrier.

2. The rate of circulation of the oxygen carrier between the air and the fuel reactor is inversely proportional to the mass of oxygen that is captured by the oxygen carrier during a cycle.

Depending on the metal oxide and fuel used, reaction (1) is often endothermic, while reaction (2) is exothermic. The total amount of heat evolved from reactions (1) and (2) is the same as for normal combustion, where the oxygen is in direct contact with the fuel.

### 2.5 Chemical looping reforming

Chemical-looping reforming utilizes the same basic principles as chemical-looping combustion. The difference is that the products desired are not heat but synthesis gas, a mix of H₂ and CO. Therefore, the air to fuel ratio is kept low to prevent the fuel from becoming fully oxidized to CO₂ and H₂O. Chemical-looping reforming in its most basic form could be described as a process for partial oxidation of hydrocarbon fuels, where a solid oxygen carrier is used as a source of undiluted oxygen. This is favorable since it would eliminate the need for expensive and power demanding air separation.

Chemical looping reforming of fossil fuel has not only an inherent advantage of nearly zero energy consumption in capturing CO₂, but also has the ability to generate pure hydrogen. An important improvement has been reached by this technology because of the auto-thermal operation that could be achieved in the CLR instead of high external heat demand required in traditional SMR reactors.

As an alternative way for hydrogen production with CO₂ capture, CLR can substitute the SMR reactors of the traditional processes, and the outlet stream of the CLR is sent to WGS reactors and a PSA unit for pure hydrogen production, as it is possible to see in figure 2.12.

Moreover, the furnace for external heating of the SMR reactors is substituted by oxygen carrier circulation within the chemical looping system. With this concept only depleted air is emitted. The auto-thermal reactor unit eliminates the use of an external heating system as well as a unit for CO2 capture from the furnace exhaust stream, reducing the energy penalty associated with these units. The use of CLR also allows the separation of the CO2 rich stream at high pressures reducing the CO2 compression costs. The main goals related to this technology are: pure hydrogen production, auto-thermal operation and CO₂ capture.
Figure 2.12 Schematic representation of chemical looping reforming

The chemical looping reforming process has a number of important advantages:
- only one gaseous component, $H_2$, needs to be separated.
- compared to the normal gas boiler used in conventional steam reforming, the temperature around the tubes is considerably lower and more uniform. The lower temperature means that a greater fraction of the combustion heat is used for steam reforming, with the consequence that the reforming efficiency is increased.

For the fluidized bed systems outlined above, important criteria for a good oxygen carrier are the following:
- high reactivity with fuel and oxygen, and ability to convert the fuel fully to $CO_2$ and $H_2O$
- low fragmentation and attrition, as well as low tendency for agglomeration
- low production cost and preferably being environmentally sound
- sufficient oxygen transfer capacity

This novel technology is based on the circulation of a solid within two different reactors operated at different conditions. The solids circulation rates determine the well performance of the reactor concept. An important aspect of circulating systems is the ability to control the solid circulation rate. One of the important factors which control the circulation rate of solids is the superficial gas velocity in the bed since this directly determines the flow regime and the density of the bed. This concept will be examined in depth in the third chapter.

2.6 Advantages and disadvantages of circulating fluidized bed

The advantages of internal circulating fluidized bed are:
- Improved gas-solid contacting given the lack of bubbles
- Reduced axial dispersion of gas
• Reduced cross-sectional area given the higher superficial velocities
• Potentially more control over suspension to wall heat transfer because of the ability to use the solids circulation flux as an additional variable
• No region like the freeboard region of low-velocity beds where there can be substantial temperature gradients
• Less tendency to show particle segregation and agglomeration
• Recirculation loop provides a location where a separate operation can be carried out
• Easier to have staged processes
• Because of superior radial mixing, fewer solids feed-points are needed
• Higher solids flux through the reactor

While the disadvantages are:

• Increased overall reactor height
• Higher capital cost
• Decreased suspension to-wall heat transfer coefficients for given particles
• Somewhat more restricted range of particle properties
• Added complexity in designing and operating recirculating loop
• Increased particle attrition

### 2.7 Membrane assisted chemical looping reforming

The Membrane Assisted-Chemical looping reforming technology is based on the concept of chemical looping. In particular it combines the advantages of FBMR and CLR. The fuel reactor is a bubbling fluidized bed with membranes inside and it is fed with methane and steam at high pressure and temperature in the range of 500-700 °C. The SMR reaction can occur because the heat required is provided by the circulation of an oxygen carrier, generally Ni-based, which acts also as catalyst. In the fuel reactor a partial combustion of the fuel takes place and for this reason it is important to feed a shortage of oxygen in order to avoid complete combustion. The oxygen carrier is subsequently circulated to the air reactor where it is oxidized with air via an exothermic reaction and the hot regenerated material is ready to start a new cycle. In this way it is possible to have an auto-thermal process due to partial oxidation of fuel, avoiding external burners.
Figure 2.13 Membrane assisted chemical looping reforming configuration

The H₂ produced in the fuel reactor is directly recovered via hydrogen-selective membranes in one single step and this contributes to shift the equilibrium towards the products increasing methane conversion. For this reason the retentate is mainly composed by CO₂ and H₂O with a very low amount of unconverted species and since the combustion takes place with pure O₂ provided by the oxygen carrier and not with air, the CO₂ is not diluted with N₂. As in the FBMR system CO₂ separation can be done simply condensing the water with low energy consumption. The main drawback of the system is the difficulty in building interconnected reactors working at high pressure: a minimum not calculated pressure drop could cause a bad solid circulation, with problems in controlling the temperature of the system.

2.8 Comparison between membrane assisted-chemical looping reforming and membrane fluidized bed reactor

MA-CLR is the best for efficient, lower emissions and investment costs due to the higher hydrogen production connected to this kind of reactor.

The main disadvantage of membrane assisted-chemical looping reforming is the difficulty in pressurized the system in order to obtain hydrogen at the pressure that the company and refinery desired.

It is not so easy working with pressurized chemical looping because the pressure fluctuations between air and fuel reactors become higher so the gas is able to go from higher to lower pressure pushing the solid and altering the normal condition of solid flux. The correct solid circulation from one reactor to the other could take place, only with a precise control of pressure in the system.

High pressure operation would be very important for the membrane-assisted chemical looping reforming process in order to

- Increase the driving force across the membrane and thereby reduce the amount of membrane surface area required for a given fuel throughout
• Deliver a high pressure CO2 stream for efficient compression, transport and storage

A future development to solve this problem could be the study of membrane assisted-chemical switching reforming that eliminate the complexity of solid circulation between reactors especially at higher pressures.

2.9 The importance of solid circulation rate in chemical looping

The performance of circulating fluidized bed systems deeply depends on the hydrodynamics. Solids holdup, particle velocity and solids fluxes are three key parameters of hydrodynamics in gas–solids systems, determining the mass and energy distribution and reaction efficiency. An accurate measurement of the solid circulation rate in a chemical looping system is essential for maintaining and controlling the solid residence time, heat balance and chemical conversion rates of the oxygen carrier. Therefore, the solid circulation rate is an important parameter that can influence:

• Mixing
• Heat transfer
• Gas-solid residence time
• Chemical conversion rate

For example if the solid circulation rate is too much from the air reactor to the fuel reactor, since the reaction in the fuel reactor is slower compared to the metal oxidation in the air reactor, the steam methane reforming could be limited by kinetics and the performance of the system is decreased. At the same time if the solid circulation rate is not enough, the heat balance for the system might not be sufficient to maintain the reforming reaction in the fuel reactor.

In order to understand better the importance of solid circulation rate in chemical looping systems, a pilot plant using a nickel-based oxygen carrier in literature is used to study the connection between oxygen carrier and heat flux from nickel oxidation [4]. The pilot plant used for the present study is designed according to Figure 2.14 with an air reactor 4.1 m high, 0.15 m inner diameter and a fuel reactor 3.0 m high and 0.16 m inner diameter.

Figure 2.14 The dual circulating fluidized bed reactor concept for chemical looping processes (LS-loop seal fluidized with steam)
The chemical looping plant operates with a design fuel power of 120 kW. The solids circulation rate and oxygen carrier are described in the table 2.1 that it necessary for energy balance.

**Table 2.1 Inlet and outlet flux in the air reactor**

<table>
<thead>
<tr>
<th>Air reactor</th>
<th>kg/s inlet</th>
<th>kg/s outlet</th>
<th>[mol/s] inlet</th>
<th>[mol/s] outlet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>0.418</td>
<td>0.372</td>
<td>7.207</td>
<td>6.414</td>
</tr>
<tr>
<td>O2</td>
<td>0.029</td>
<td>0</td>
<td>0.909</td>
<td>0</td>
</tr>
<tr>
<td>NiO</td>
<td>0.122</td>
<td>0.180</td>
<td>1.649</td>
<td>2.435</td>
</tr>
</tbody>
</table>

The main hypothesis for which the calculations are done are:

- Stationary conditions of chemical equilibrium
- All the oxygen is completely absorbed in Nickel particles since the temperature is higher than 900 °C
- There are no external dispersions

In order to calculate the heat released from the oxidation, it is necessary to consider the enthalpy balance of the system according to equation (1) and (2).

\[
H_{IN}(n_{IN},T_{IN}) - H_{OUT}(n_{OUT},T_{OUT}) + Q = 0 \tag{1}
\]

\[
H_i(n_i,T_i) = \Delta H^0_f, (298 \text{ K}) + \int_{298K}^{T} c_{P,i} \, dT \tag{2}
\]

Where a stream of ideal gas can be obtained as sum of specific enthalpy of every component that compose the molar flux of the system as it is described in equation (3)

\[
H(T) = \sum_{i=1}^{NC} n_i \cdot H_i(n_i,T_i) \tag{3}
\]

\(c_{P,i}\) depend on the element of the gas and is a polynomial function of temperature and for the case of nickel, oxygen and nickel oxide can be written according to equation (4), (5) and (6).

\[
c_{P,Ni} = 6.99 + 0.000905 \cdot T \quad \frac{cal}{mol \cdot K} \tag{4}
\]

\[
c_{P,NiO} = 11.3 + 0.00215 \cdot T \quad \frac{cal}{mol \cdot K} \tag{5}
\]

\[
c_{P,O2} = 8.27 + 0.000258 \cdot T - \frac{187700}{T^2} \quad \frac{cal}{mol \cdot K} \tag{6}
\]

Solving the equation, the total power is equal to \(Q = 145,909 \text{ kW}\).

The temperature considered are the respectively the inlet and outlet temperature of the air reactor equal to 900°C and 1000°C. If the solid circulation rate is changed, the heat required also becomes different, as it is possible to see in figure 2.15.
### Table 2.2 Inlet and outlet molar flux in the air reactor for reference case

<table>
<thead>
<tr>
<th>Air reactor</th>
<th>kg/s inlet</th>
<th>kg/s outlet</th>
<th>[mol/s] inlet</th>
<th>[mol/s] outlet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>0.418</td>
<td>0.372</td>
<td>7.207</td>
<td>6.414</td>
</tr>
<tr>
<td>O2</td>
<td>0.029</td>
<td>0</td>
<td>0.909</td>
<td>0</td>
</tr>
<tr>
<td>NiO</td>
<td>0.122</td>
<td>0.180</td>
<td>1.649</td>
<td>2.435</td>
</tr>
</tbody>
</table>

### Table 2.3 Inlet and outlet molar flux in the air reactor for all the cases analyzed

<table>
<thead>
<tr>
<th>NiO [mol/s] inlet flux</th>
<th>NiO [mol/s] outlet flux</th>
<th>Difference NiO inlet and outlet flux</th>
<th>Q [kW]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.473</td>
<td>7.703</td>
<td>2.23</td>
<td>410458</td>
</tr>
<tr>
<td>4.23</td>
<td>6.162</td>
<td>1.932</td>
<td>335551</td>
</tr>
<tr>
<td>1.838</td>
<td>2.892</td>
<td>1.054</td>
<td>199085</td>
</tr>
<tr>
<td>1.649</td>
<td>2.435</td>
<td>0.786</td>
<td>145069</td>
</tr>
<tr>
<td>1.49</td>
<td>1.92</td>
<td>0.43</td>
<td>126818</td>
</tr>
</tbody>
</table>

**Figure 2.15 Trend of heat flux with solid circulation rate**

From enthalpy balance it is possible to see there is a strong connection between the solid circulation rate and the heat flux going from air reactor to fuel. In table 2.2 and table 2.3 are described all the cases analyzed, obtained changing the molar flux in the reactor in order to respect the molar balance of the system. It is possible to see that using the same thermodynamic conditions but changing the NiO flux going to the fuel reactor, the heat flux is quite different. This example can explain the real importance to predict the solid circulation rate because is a relevant parameter that can change the behavior of fuel reactor.
Chapter 3

Experimental methods

3.1 Setup and design of experiments

This work has the purpose to analyze different techniques for the measurement of SCR for Chemical Looping. The work focuses on the comparison of three different experimental methods for predicting SCR, either intrusive or non-invasive [16,17]. To study the solid circulation rate, a pseudo 2D reactor, described in figure 3.1, is used for the measurements. The internal column is a riser reactor and works as the air reactor in Chemical Looping systems, while the two external columns represent the fuel reactor in Chemical Looping and operate in the bubbling regime.

The riser is the driving force for the solids circulation because the particles circulate from the top of the riser to the external columns, which are 7.0 cm in width. The riser operates in the fast fluidization regime well above the terminal velocity of the particles. Solids circulate from the bottom of the external columns to the top of the riser.
riser through two orifices with an internal diameter of 1.5 cm placed 15.2 cm above the distributor of the central column. The fact that a high pressure drop is created at these holes since the bed near holes behaves like a moving bed, avoids the gas leakage from the fuel reactors to the riser. On top of the riser there is an impact element which reduces the velocity of the particles in such way that the gas is forced to follow a trajectory out of the reactor while particles fall to a chamber connected to the fuel reactors through a 2.0 cm hole where particles move from the riser to the fuel columns. Again gas leakage from fuel reactor to the riser is avoided due to the fact that solid is accumulated in this chamber near the holes.

For all experiments air is used as inlet gas in each column and is fed through a porous plate with mean pore size of 40 μm. The front wall of the bed is made of glass in order to capture images while the background wall is kept anodized black in order to help particle detection when using optical techniques like PIV/DIA. In the reference case, a solids inventory of 2 kg of glass beads particles belonging to Geldart B with a size distribution of 400-600 μm is used. In the picture 2.7 there are colored dots that represent the point in which particles used are in the Geldart classification. Glass beads particles with a mean diameter of 500 μm have a minimum fluidization velocity equal to 0.21 m/s, with 388 μm is 0.144 m/s while with 250 μm is equal to 0.095 m/s. For sand the minimum fluidization velocity is 0.133 while for alumina is 0.162 m/s. The minimum fluidization velocity $u_{mf}$ is calculated by the standard pressure drop method, while their terminal velocity is calculated according to the correlation by Kunii and Levenspiel [1]. For all the experiments in this work, the minimum fluidization velocity and terminal velocity of all the particles are calculated before starting it.

A 0-1000 l/min mass flow controller is used in the riser, while the inlet gas flow rates in the fuel columns are controlled by a 0-50 l/min mass flow controllers, all supplied by Brooks Instruments. In order to prevent electric static charging of the particles, water tanks are used in each inlet line to humidify the air. The properties of the base case used in this work are described in table 3.1. In order to study the SCR, more experiments with different experimental conditions have been used, changing gas flow rates, solids inventories, particle types and particle diameters as stated in table 3.2. Furthermore, the developed methods have also been extended to non-spherical particles, where the determination of SCR becomes more difficult due to the lack of homogeneity as compared to spherical beads. In this work, particle sphericity has been measured for non-spherical particles using an Expert Shape Quantachrome machine.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>abr.</th>
<th>dimension</th>
<th>Fuel vessel</th>
<th>Air vessel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particles</td>
<td>-</td>
<td>-</td>
<td>glass beads</td>
<td></td>
</tr>
<tr>
<td>particle diameter</td>
<td>$d_p$</td>
<td>[m]</td>
<td>5.00.10$^{-4}$</td>
<td></td>
</tr>
<tr>
<td>particle density</td>
<td>$\rho_s$</td>
<td>[kg/m$^3$]</td>
<td>2500</td>
<td></td>
</tr>
<tr>
<td>inlet gas</td>
<td>-</td>
<td>-</td>
<td>air</td>
<td>air</td>
</tr>
<tr>
<td>gas density</td>
<td>$\rho_g$</td>
<td>[kg/m$^3$]</td>
<td>1.184</td>
<td>1.184</td>
</tr>
<tr>
<td>Dynamic viscosity</td>
<td>$\mu_g$</td>
<td>[Pa*s]</td>
<td>1.79$\cdot$10$^{-5}$</td>
<td>1.79$\cdot$10$^{-5}$</td>
</tr>
<tr>
<td>Superficial gas velocity</td>
<td>$u_g$</td>
<td>[m/s]</td>
<td>0.32</td>
<td>2.94</td>
</tr>
<tr>
<td>Gas flow rate</td>
<td>$F$</td>
<td>[ln/min]</td>
<td>1.66 $u_{mf}$</td>
<td>15 $u_{mf}$</td>
</tr>
<tr>
<td>Solids Inventory</td>
<td>SI</td>
<td>[kg]</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Sphericity</td>
<td>$\varnothing$</td>
<td>[-]</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>
Table 3.2 List of the experiments for solid circulation rate measurement

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Solids inventory (SI) [kg]</th>
<th>Particles</th>
<th>(d_p) [μm]</th>
<th>(\rho_p) [kg/m(^3)]</th>
<th>(\varnothing) [-]</th>
<th>(U_{in}/U_{mf})</th>
<th>(U_{ar}/U_{mf})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.0</td>
<td>Glass beads</td>
<td>500</td>
<td>2500</td>
<td>1</td>
<td>1.66</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>2.0</td>
<td>Glass beads</td>
<td>500</td>
<td>2500</td>
<td>1</td>
<td>1.66</td>
<td>17</td>
</tr>
<tr>
<td>3</td>
<td>2.0</td>
<td>Glass beads</td>
<td>500</td>
<td>2500</td>
<td>1</td>
<td>1.66</td>
<td>13</td>
</tr>
<tr>
<td>4</td>
<td>2.0</td>
<td>Glass beads</td>
<td>500</td>
<td>2500</td>
<td>1</td>
<td>1.30</td>
<td>15</td>
</tr>
<tr>
<td>5</td>
<td>2.0</td>
<td>Glass beads</td>
<td>500</td>
<td>2500</td>
<td>1</td>
<td>2.00</td>
<td>15</td>
</tr>
<tr>
<td>6</td>
<td>2.25</td>
<td>Glass beads</td>
<td>500</td>
<td>2500</td>
<td>1</td>
<td>1.66</td>
<td>15</td>
</tr>
<tr>
<td>7</td>
<td>2.5</td>
<td>Glass beads</td>
<td>500</td>
<td>2500</td>
<td>1</td>
<td>1.66</td>
<td>15</td>
</tr>
<tr>
<td>8</td>
<td>2.0</td>
<td>Glass beads</td>
<td>250</td>
<td>2500</td>
<td>1</td>
<td>2.00</td>
<td>24</td>
</tr>
<tr>
<td>9</td>
<td>2.25</td>
<td>Glass beads</td>
<td>250</td>
<td>2500</td>
<td>1</td>
<td>1.70</td>
<td>24</td>
</tr>
<tr>
<td>10</td>
<td>2.5</td>
<td>Glass beads</td>
<td>250</td>
<td>2500</td>
<td>1</td>
<td>1.40</td>
<td>24</td>
</tr>
<tr>
<td>11</td>
<td>2.25</td>
<td>Glass beads</td>
<td>388</td>
<td>2500</td>
<td>1</td>
<td>1.66</td>
<td>15</td>
</tr>
<tr>
<td>12</td>
<td>2.25</td>
<td>Glass beads</td>
<td>388</td>
<td>2500</td>
<td>1</td>
<td>1.66</td>
<td>16</td>
</tr>
<tr>
<td>13</td>
<td>2.25</td>
<td>Glass beads</td>
<td>388</td>
<td>2500</td>
<td>1</td>
<td>1.66</td>
<td>17</td>
</tr>
<tr>
<td>14</td>
<td>2.0</td>
<td>Sand</td>
<td>460</td>
<td>2600</td>
<td>0.75</td>
<td>1.35</td>
<td>14</td>
</tr>
<tr>
<td>15</td>
<td>2.0</td>
<td>Sand</td>
<td>460</td>
<td>2600</td>
<td>0.75</td>
<td>1.35</td>
<td>14</td>
</tr>
<tr>
<td>16</td>
<td>2.0</td>
<td>Sand</td>
<td>460</td>
<td>2600</td>
<td>0.75</td>
<td>1.35</td>
<td>15</td>
</tr>
<tr>
<td>17</td>
<td>1.3</td>
<td>Activated alumina</td>
<td>510</td>
<td>1135</td>
<td>0.776</td>
<td>1.2</td>
<td>14</td>
</tr>
<tr>
<td>18</td>
<td>1.3</td>
<td>Activated alumina</td>
<td>510</td>
<td>1135</td>
<td>0.776</td>
<td>1.4</td>
<td>14</td>
</tr>
<tr>
<td>19</td>
<td>1.3</td>
<td>Activated alumina</td>
<td>510</td>
<td>1135</td>
<td>0.776</td>
<td>1.2</td>
<td>15</td>
</tr>
</tbody>
</table>

For the first seven experiments, glass beads particles with a diameter of 500 μm were used. In the first five experiments, in order to study the influence of gas velocities in the solid circulation rate, the same solids inventory equal to 2 kg was used, while the velocity in the air reactor was changed in the first three experiments and the velocity in the fuel reactor was changed in the other two. Experiments six and seven were carried out to study the effect of solids inventory.
In the consecutive other three experiments, the size of particles was reduced to 250 μm in order to study the effect of solids inventory and in the later three experiments, the particles size was increased to 388 μm in order to see the effect of particle size with a bigger dimension of particles.

In the next three experiments the sand particles with a mean diameter of 460 μm were used in which the influence of sphericity was analyzed, while in the last three experiments activated alumina particles were used in order to study the effect of density and sphericity.

In order to check the size distribution of the particles, a sample was analyzed in a machine able to recognize the percentage of particles for every different size and to measure the average as it is possible to see in the figure 3.2. The distribution of every samples is a flat distribution, with the pick in correspondence of the average diameter.
3.2 Methods to calculate the solid circulation rate

Solid circulation rate is an important parameter for chemical looping because it is able to control the reaction of steam methane reforming influencing the heat transfer and the solid residence time. It is important to find a way that allow the measurement of the solid circulation rate for the 3D reactor in order to know the solid flux between the air and fuel reactor without stopping the reaction as it happens in the collecting particles method. Three methods are known from literature, but only the pressure method is able to not interrupt the system in a real reactor.

To the measurement of solid circulation three different methods are used: collecting particles, pressure transducer and optical technique. Pressure transducers are used along the riser in order to determine solids holdup and solids velocities while the optical technique is a non-intrusive experimental method which consists in taking images of the reactor to study its hydrodynamics. The technique combines Particle Image Velocimetry (PIV) for a proper estimation of particle velocities with Digital Image Analysis (DIA) for the determination of solids holdup at any position in the bed and their combination provides information on the solid fluxes of the particles that are going from the riser to the fuel reactor. The main problem of this technique is that it can be used only in a 2D reactors to allow capturing images.

The optical technique has been already applied in fluidized beds systems and in this study it is extended to the chemical looping system for the first time for the non-invasively measurement of the SCR.

3.2.1 Collecting particles method:

The collecting particles method consists in collecting particles in an external bucket and subsequently weight it by know the opening time for solids collection. To study this phenomenon two windows in the fuel columns are substituting with windows with holes in order to allow the particles from the riser to the fuel columns going through the holes and being collected in a container. The procedure for the measurement consists in maintaining the gas velocity below its terminal velocity, so particles remain in the riser. Then the velocity in the riser is increased until the real operative condition for each experiment described in table 3.2 and after
a short time, that will be explained deeply after, the inlet gas velocity in the riser is again reduced below the terminal velocity. The timer is started when particles exit through the hole and get collected in a bucket and it is stopped when the last particles pass through the hole. The short interval of time in which the timer is used was studied in detail in order to avoid modification of the system. The solids inventory in the reactor, as it will be explained better in the next chapter, can influence the solid circulation rate; it means it is really important the time does not become longer in order to avoid decreasing of solid circulation rate that could disturb the system.

Prior measuring solids circulation rates for the different experiments, it is important to assess reproducibility of the measurements when collecting particles. The first experiment was repeated changing the interval of time in which the particles were collected in order to understand this effect. In the figure 3.3 the results of this study are presented, where it is possible to note a decrease of solid circulation rates when the collecting time is increased. This result is explained by the exceedingly change in the solids inventory when collecting particles for a long period. According to these discovery, the collecting time used, should not be higher than 15 seconds in order to not disturb the hydrodynamics of the system. After this first analysis, all the experiments are conducted in such a way that the system is affected as less as possible and representative results are achieved. For every case, results of solid circulation rate are obtained through an average of 15 measurements. This method is the most accurate compared with the others because it consists really in collecting the particles but the main disadvantage is related to the fact that in chemical looping the system must be interrupted to collect particles.

![Figure 3.3 Influence of the collecting time on solid circulation rate.](image-url)
3.2.2 Optical technique

The second method is the optical technique called PIV-DIA, which is based on recording images with a high speed camera and then analyzed with a cross correlation method. In this study a Dantec Dynamics Flowsense EO 16M camera is used for PIV-DIA analysis in the 2D column, which provides a maximum resolution of 4872 x 3248 pixels. Two images are taken in double frame mode with a very short interval of 0.5 ms, followed by a longer interval of 0.5 s before the next two pictures are recorded. The pictures are subsequently analyzed by the software DynamicStudio that processes the images. In this way, the two consecutive images can be analyzed together in order to get the information of the hydrodynamics of the bed. Two LED lights are used to illuminate the system as it is possible to see in the picture 3.1. A trigger connected to the computer controls the camera shutter and a resolution of 3 pixels per particle is used during the recordings, always at 8 bits depth for double frame mode.

For the measurement of SCR with this technique, only a part of the reactor in which all particles in the fuel columns are coming down, while in the riser mainly up but also down near the wall, because of the wall. The main advantage of this system consists in the fact that the sum of solid circulation rate in the fuel columns is equal to the slid circulation rate in the riser. This area is located 80 cm from the bottom, it is 20 cm in height of the reactor and covers all the width that is 23 cm.

The technique consists first in Particle Image Velocimetry for measuring the particle velocities and subsequently in Digital Image Analysis for the determination of solids particles holdup. Their combination provides information on the solid fluxes going from the riser to the fuel reactor.

Particle Image Velocimetry is a widely used experimental technique for the measurement of solids motion in pseudo 2D fluidized beds. PIV/DIA has been selected for this experimental study due to its simplicity, its non-intrusiveness and the detailed whole-field information on both gas and emulsion phase with high spatial and temporal resolution that this technique can give. This technique can provide an accurate quantitative measure of the instantaneous flow velocity field across a planar area of a flow field as it is possible to see in figure 3.4.

![Figure 3.4 General setup of a 2D PIV system](image)

Images recorded are subsequently analyzed using first PIV. This technique gives information on the instantaneous flow velocity across a planar area. The software used in this work for PIV is Davis 8.0 that divides the images into interrogation areas and then applies cross correlation algorithms in order to get the most probable displacement of the solids confined in that interrogation area. The algorithm computes the
cross-correlation between the two frames to get average displacement of the particles and gives a velocity vector which is the most likely displacement one. All vectors in the interrogation areas are plotted and the instantaneous macroscopic flow pattern is obtained.

The software Davis 8.0 is based on three main operations. In the first step it subtracts a “background” intensity map to the raw images in order to minimize inhomogeneous illumination effects along the bed. In this operation, it is taken first a picture of the empty columns of the reactor in order to subtract the noise. The second operation (create multi-frame buffer from time series) receives the two consecutive picture and then put together in order to obtain a single frame that could be analyzed to understand the movement of every particles. The last operation is based on image preprocessing, vector calculation parameter and vector postprocessing. The option “image preprocessing” allow the particle intensity normalization which apply a local particle intensity correction. This is especially useful when working on particle images with a high intensity fluctuations, due to inhomogeneous particle diameter.

As a result it obtain homogeneous particle intensities so that small particles will also contribute to the correlation.

The vector calculation parameter allow to select the data source and the mode of correlation which can be done in a single step or iteratively via multi pass.

The standard cross-correlation PIV algorithm computes first the 2D-cross correlation plane from the correlation of the two input image interrogation windows $I_1$ and $I_2$ from the light exposure at two different times shortly after another.

The correlation plane of size nxn pixel at image position is defined as:

$$ C(x_0, y_0) = I_1(t_1, x_0, y_0) * I_2(t_2, x_0, y_0) $$

Then in the correlation plane the highest correlation peak is detected, whose positions corresponds to the most likely displacement of the particle ensemble in the interrogation window.

Vector $V(x_0, y_0)$ is the position of highest peak in $C(x_0, y_0)$.

Each cross-correlation of a single pair of interrogation windows leads to a single displacement of the particle vector. All vectors together are then combined to yield a complete 2D-vector field of the whole image.

A large number of images are acquired and the corresponding vector fields are computed and the vector fields are locally averaged to compute an average vector field:

$$ V_{avg}(x_0, y_0) = \frac{\sum V(x_0, y_0)}{n} $$

With n=number of images/vector fields.

![Figure 3.5 Evaluation of PIV recordings using Auto-Correlation](image)
For the evaluation of images via correlation the complete image is divided in so-called interrogation windows. The correlation function operates on the intensities inside each interrogation window and passes through the complete PIV recording with a specified window shift. The evaluation yields one velocity vector for each interrogation window. The correlation selected is the cross correlation that calculates a vector field on two single-exposed images. The original images consists of two-frames, so the algorithm computes the cross-correlation of all interrogation windows between the first and second frame.

In the multi pass iterations, the vector field is calculated by an arbitrary number of iterations with a decreasing interrogation window size. The initial interrogation area is of 128 x 128 px, while in the second pass the interrogation area is decreased to 64 x 64 px.

The evaluation starts in the first pass with the initial interrogation window size and calculates a reference vector field. In the next pass the window size is half the size of the previous pass and the vector calculated in the first pass is used as a best choice window shift.

This ensures the same particles are correlated with each other even if it uses small interrogation windows. The overlap defines the overlap among neighboring interrogation windows. The bigger the specified overlap, the closer is the grid of computed velocity vectors.

The interrogation window size and the window overlap determine the grid size of a vector field. With a window size of 64 x 64 pixel and an overlap of 50% give a grid size of 32 x 32 pixel.

The next step of PIV is the multi-pass options that allow to enter a suitable initial shift in order to enhance the signal-to-noise ratio of the correct correlation peak. The default constant value for the shift is dx=0 and dy=0. Using this shift the particle image is reconstructed in a first step and the corresponding interrogation windows are positioned symmetrically around the position of the final vector.

In the picture 3.6 the original image and the consequent velocity vector are shown. PIV only accounts for the particles that are inside the interrogation zone in a 2D plane. Therefore particles that move out of interrogation zone are not taken into account. The error caused by this drawback is minimized by a short interval between two pictures. Double frame mode minimizes this error by taking two consecutive images with a very short interval.

Figure 3.6 Original image and image after Davis modelling
PIV analysis only provides information on the particle velocities. To determine the solid holdup and the solid flux profiles another post-processing technique is used: Digital Image Analysis. DIA is an in-house software developed with the image processing toolbox in Matlab. In this technique, every image is divided into interrogation zones in which the normalized pixel intensity is used to get the bed porosity. This value obtained is the 2D solids fraction. In this case the 2D pixel intensity is correlated to 3D porosity using the correlation suggested by de Jong [2], which was developed for fluidized beds as it will explained later [23]. However, solids hold-up in this system are much lower than in fluidized beds because the fuel columns are a dilute system compare to the fluidized bed, so a new correction method from planar 2D intensities to reliable 3D solids hold up has been developed in this work.

Before finding the 3D solids hold up, inhomogeneous lighting in the different set of experiments is corrected. Since in the fuel column the solid holdup is much lower compared to the riser, they are more affected by inhomogeneous lights, so it was necessary to find a way in order to correct this problem. Another important reason to correct the illumination is related to the fact that the method should be reproducible but differences in illumination can affect the results of solid circulation rate. Two different method to correct the inhomogeneous lighting are proposed: the fixed and dynamic methods. The first was used for fuel columns and the second for the riser.

In the first, the bed is filled with particles and images are taken to the fixed bed, which is subsequently used as background for normalization of every single image of the experiment. In this method the lighting for the background image and the corresponding to the experiments should be exactly the same because if the purpose is to correct the difference in illumination, it is necessary that the camera and LED lights are exactly in the same position. This correction is shown in figure 3.11, where the average histograms of two different recordings in the right side of the fuel column are depicted before and after normalization by the fixed bed image. Both histograms correspond to operation conditions of experiment 8 but with completely different initial illuminations. In figure 3.8, it is observed how for different illuminations, the fixed bed background correction method is able to normalize the intensities, which would lead to reproducibility of the measurements. The importance of this method is related to the possibility to obtain the same results of solid circulation with the same operative conditions but with different illumination. The figure shows the background correction that is like a packed bed, without fluidization. The histogram shows two tests of illumination that were taken before the experiments, in which is possible to see that even if the starting illumination is different, the results are not affected from this, while for the method without background correction, this is not true. These tests are related to the same case but in which the left and right parts of the reactor were not lighted up with the same illumination, but the histogram of the left part was lower compare to the right. The method without background correction is not able to solve the difference in illumination, while the method with background correction, using the ratio between the original image and the background could adjust the difference. In the case without background correction, the difference of solid circulation rate in the left and right part of the fuel reactors, was higher than in the case with background correction. It means that the background correction could be use with different illuminations but the results will still be the same, while it is not possible without background correction, where the illumination affects a lot the results. A picture that shown the background image used to subtract the original image is described in figure 3.7
For the riser vessel, which is less diluted than the fuel vessels, the background image used for the correction of inhomogeneous lighting is obtained by averaging all images of the recorded experiment, which represents the dynamic background method. Subsequently, every image is normalized by the subtraction of this average background image.

In previous studies the background optimization was analyzed. Two different steps involve the background correction in order to get accurate results: first the background determination and then the background subtraction for every image. These two have a big influence on the results and it is why they were carefully studied. Due to solids circulate downwards near the walls in the fuel reactors 3.9a, a highly concentrated region is observed in that part for the background image 3.9b. Once this image is subtracted for every image, a clear mismatching between real
measurements in the porosity measured is observed 3.9d which leads into an erroneous solid flux profile 3.9e. As already mentioned, this system works for fluidized beds, where the emulsion phase occupies a great part of the image.

Figure 3.9 Plots obtained in DIA analysis with the usual background correction.

The failure of the previous background correction is mainly related to the high values obtained in the region where particles are descending. In order to solve this problem it has been proposed the normalization of the intensities measured after the background determination. In this way, the background image will smooth every image and will not subtract real information.

Figure 3.10 Plots obtained in DIA analysis with the background correction including normalized background from 0 to 1.

However, a well performance of this method is only obtained when during the PIV post processing some data is set to a threshold value in order to avoid big differences in intensity. For that reason a new background determination method has been proposed. This novel method includes a normalization of the image from 0 to 1. Then, the minimum value of intensity from the emulsion phase is subtracted to the normalized image in order to have an intensity of 0 where there are normally no particles. Finally, the image resulting of the previous operations is divided by the mean intensity value from the emulsion phase. This method involves to remove the PIV operation consisting to set above or below some values to constant, in order to avoid a loss of data in the background correction.
For all the background correction this third method studied in the literature was used. Once images have been normalized and corrected by inhomogeneous lighting, a correlation between the pixel intensity that is the 2D solids fraction and the actual porosity 3D porosity should be used.

In the previous work of Jong, solid circulation rate was studied for FBR and the equation (1) was found.

\[
\begin{align*}
\varepsilon_{3D} &= \begin{cases} 
A \frac{\varepsilon_{2D}}{1 - \frac{1}{B} \varepsilon_{2D}} & \text{for } \varepsilon_{3D} < \varepsilon_{3D,max} \\
\varepsilon_{3D,max} & \text{for } \varepsilon_{3D} \geq \varepsilon_{3D,max}
\end{cases} 
\end{align*} \quad (1)
\]

Where A and B are parameters influencing the initial and final slope of the curve, while \(\varepsilon_{2D}\) is the 2D porosity, and \(\varepsilon_{3D}\) is the real one and it is described in picture 3.12.

Figure 3.11 Plots obtained in DIA analysis with the third model of background correction

Figure 3.12 Correlation connecting porosity 2D to porosity 3D
The relative bed depth $\Delta z/d_p$ is expected to affect the parameters $A$ and $B$ as the table 3.3 shows, but printout $A$ and $B$ are good only for FBR because in chemical looping and riser, the maximum porosity decreases and the curve is moved under. The parameter values from table are not suitable for this case because they were calculated for a fluidized bed reactor and not for a diluted system like the ICFB reactor. The most important parameter affecting $A$ and $B$ is the bed depth meanwhile a change in particle size and $u/umf$ give similar results of $A$ and $B$. With $\Delta z/d_p$ higher than 20, there is a vertical asymptote in the curve. For the all cases considered in the experiments the bed depth is always higher than 20.

In such diluted systems like the ICFB, a linear correlation between the intensity and porosity is proposed in equation 2. The value of $A$ has been first fitted based on the SCR measured by collecting particles for the first five experiments and has subsequently been applied for all the experiments done. First the PIV-DIA method without background correction was applied, and only after when it was clear that the difference in illumination could influence the solid circulation rate, the background fixed correction was used in the fuel reactors. For all cases the SCR are calculated by averaging the actual solid fluxes measured through the combination of velocity with PIV and porosity with DIA at every axial position in the image.

$$\varepsilon_{3D} = A \cdot \varepsilon_{2D} \quad (2)$$
3.2.3 Pressure transducers methods

The third method is based on pressure transducers that allow to measure the pressure drop over the riser. The setup is composed of 8 transducers connecting at different height of the riser in order to obtain the pressure profile of the reactor with the height.

The main aim of this method is to determine the total pressure drop of the riser $\Delta P_{\text{riser}}$ between the top and the bottom. This pressure drop allows the estimation of the solid circulation rate in the riser as a function of the local solids holdup measured. For a proper measurement of SCR using the pressure drop method is important the location of the pressure transducers in order to get a good description of the behavior of the bed. These pressure transducers have been located at specific positions in the bed as it is possible to see in figure 3.13.

![Figure 3.13 Pressure transducer setup](image)

To determine the solid circulation rate, it needs to know the particle velocity and solid holdup according with the equation:

$$SCR = u_p \ast \varepsilon_S \ast A \ast \rho_s$$

Where $u_p$ is the particle velocity, $\rho_s$, the density of the particle, $\varepsilon_S$ is the solid holdup and $A$ the section of the riser.

To calculate the solid holdup and the particle velocity, the model of Richardson and Zaki for mono-component suspension, in system with the Bernoulli equation, was used.

The basic assumptions of the system are:
• The system is composed of spherical particles of common specific gravity with a relatively narrow size distribution which can be reduced to an average characteristic size.
• There are no interactions of any kind between the particles, except hydrodynamic effects through the fluid.
• The relative positions of the particles in the cloud are completely random, without any segregation.
• The effect of the walls of the container is neglected.

The equations in the system (2) are the Bernoulli equation and the Richardson and Zaki equation.

\[
\begin{align*}
    u_p &= \frac{u_g}{(1 - \varepsilon_S)} - u_t \ast (1 - \varepsilon_S)^{n-1} \\
    \frac{p_2 - p_1}{\rho_R} - g \ast (h_2 - h_1) &= 4 \ast F \ast \frac{L}{D} \ast \frac{1}{2} \ast (u_g + u_p)^2
\end{align*}
\]

Where \(F\) is the fanning frictional factor, \(u_g\) the superficial velocity of the gas, \(u_t\) the terminal velocity of particles, \(p_2 - p_1\) is the pressure drop calculated with the transducers and \(\rho_R\) the density in the riser calculated according to equation (3)

\[
\rho_R = \rho_S \ast \varepsilon_S + \rho_G \ast \varepsilon_G
\]

Where \(n\) is calculated in accordance with equation (4)

\[
n = \left(4,45 + 18 \ast \frac{d_p}{D}\right) \ast Re_t^{-0.1}
\]

The terminal particle velocity is based on equation (5) for spherical particle:

\[
u_t = \left(\frac{4 \ast d_p \ast (\rho_s - \rho_g) \ast g}{3 \ast \rho_g \ast C_D}\right)^{\frac{1}{2}}
\]

Where \(C_D\) is the drag coefficient, \(\varepsilon_S\) and \(\varepsilon_G\) are respectively the porosity of the solid and of the gas, while \(\rho_S\) and \(\rho_G\) are the density of particle and gas. \(C_D\) is calculated according with the equation [26]:

\[
C_D = \frac{24}{Re_p} \ast \left(1 + 0,14 \ast Re_p^{0.7}\right) \text{ for } 0,1 < Re_p < 1000
\]

To calculate the frictional factor, the regime of the flow should be first determined. In every test the Reynold’s value was for turbulent regime because it was higher than 2300

\[
Re = \frac{\rho \ast v \ast D}{\mu} > 2300
\]

so it used the Colebrook-White equation [25]:
\[
\frac{1}{\sqrt{f}} = 1,14 - 2 \cdot \log_{10}\left(\frac{\lambda}{D} + \frac{9,35}{Re \cdot \sqrt{f}}\right) \quad \text{for } Re > 4000
\]

\[
f = 4F
\]

where \( f \) is the Darcy frictional factor that is 4 time the fanning frictional factor, while \( \lambda \) is the roughness of anodized aluminum that is the material of the riser. \( D \) is the hydraulic diameter for internal convection because the riser’s section is rectangular, with sides \( a \) and \( b \).

\[
D = \frac{2 \cdot a \cdot b}{a + b}
\]

### 3.2.3.1 Pressure transducer method for non spherical particles

For the case of non-spherical particles, the terminal velocity is modified and it is adjusted properly as indicated by Haider and Levenspiel [28], who implemented the equation suggested by Turton and Clark [29]. Equations 12-14 show the procedure to determine the new terminal velocity using the dimensionless particle diameter first \( (d_p^*) \), and subsequently the dimensionless terminal velocity of the particles \( (u_t^*) \) [26].

\[
d_p^* = d_p \left[\frac{\rho_g (\rho_s - \rho_g) g}{\mu^2}\right]^{1/3}
\]

\[
u_t^* = \frac{18}{(d_p^* )^2} + \frac{2,335 - 1,744 \cdot \phi}{(d_p^* )^{0.5}}^{-1}
\]

\[
u_t = u_t^* \left[\frac{\rho_g^2}{\mu (\rho_s - \rho_g) g}\right]^{-1/3}
\]

One of the main problem for non spherical particles, is related to the fact that the terminal velocity is really dependent on the spericity as it is possible to see in the figure 3.14.

![Figure 3.14 Terminal velocity and SCR trend with the spliercity](image-url)
If the sphericity is different for every particle, it means the particles are reaching the top part of the reactor with different time and the pressure fluctuation become higher. The standard deviation of the pressure drop is really important compare to the case of spherical particles.

3.3 Experimental and modelling comparison for hydrogen production in FBR and MFBR

As already said, it is very important to understand and predict the solid circulation rate in chemical looping, since it could influence the behavior of fuel reactor. As it was shown with the case study, the heat flux going from air reactor to fuel is really dependent on solid circulation rate and the heat flux govern the steam methane reforming and water gas shift in fuel reactor so can influence the conversion of methane and at least, for the case of membrane assisted chemical looping reforming, the hydrogen production. The membrane assisted chemical looping reforming system is a quite complex reactor because it consists in chemical looping and a membrane fluidized bed reactor. In order to analyze deeply this system and connect the information from solid circulation rate to the fuel reactor, the behavior of fluidized bed membrane reactor has been assessed via phenomenological models and comparison to experiments in which the main purpose is to analyze the methane conversion and hydrogen production.

The second part of the work consists in studying the comparison between FBR and MFBR with experiments and modelling in order to analyze the effect of temperature, pressure, velocity and composition. The reactor has a diameter equal to 0,045 m and a height of 0,17 m. The distance distributor to the beginning of the membrane is equal to 3 cm. The conditions for the catalyst used, that is activated nickel, are described in table 3.4 while for the membrane in table 3.5.

<table>
<thead>
<tr>
<th>Table 3.4 Operative parameters for catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Catalyst</strong></td>
</tr>
<tr>
<td>particle diameter</td>
</tr>
<tr>
<td>density</td>
</tr>
<tr>
<td>particle porosity</td>
</tr>
<tr>
<td>apparent density</td>
</tr>
<tr>
<td>surface area</td>
</tr>
<tr>
<td>sphrency factor</td>
</tr>
<tr>
<td>amount</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 3.5 Operative parameters for membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Membrane</strong></td>
</tr>
<tr>
<td>D</td>
</tr>
<tr>
<td>Length</td>
</tr>
<tr>
<td>Thickness</td>
</tr>
<tr>
<td>Pm</td>
</tr>
<tr>
<td>Ea</td>
</tr>
<tr>
<td>n</td>
</tr>
</tbody>
</table>
In order to study the effect of temperature, pressure, composition and velocity the operating conditions are described in the table 3.6, 3.7, 3.8 and 3.9.

Table 3.6 Operating conditions for analyze the effect of composition

<table>
<thead>
<tr>
<th>Exp</th>
<th>T</th>
<th>Pret</th>
<th>Pperm</th>
<th>u/umf</th>
<th>H2O [mole%]</th>
<th>N2 [mole%]</th>
<th>CH4 [mole%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>500</td>
<td>4</td>
<td>0</td>
<td>3</td>
<td>0,3</td>
<td>0,6</td>
<td>0,1</td>
</tr>
<tr>
<td>2</td>
<td>500</td>
<td>4</td>
<td>0</td>
<td>3</td>
<td>0,4</td>
<td>0,5</td>
<td>0,1</td>
</tr>
<tr>
<td>3</td>
<td>500</td>
<td>4</td>
<td>0</td>
<td>3</td>
<td>0,2</td>
<td>0,7</td>
<td>0,1</td>
</tr>
</tbody>
</table>

Table 3.7 Operating conditions for analyze the effect of temperature

<table>
<thead>
<tr>
<th>Exp</th>
<th>T</th>
<th>Pret</th>
<th>Pperm</th>
<th>u/umf</th>
<th>H2O [mole%]</th>
<th>N2 [mole%]</th>
<th>CH4 [mole%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>500</td>
<td>4</td>
<td>0</td>
<td>3</td>
<td>0,3</td>
<td>0,6</td>
<td>0,1</td>
</tr>
<tr>
<td>2</td>
<td>550</td>
<td>4</td>
<td>0</td>
<td>3</td>
<td>0,3</td>
<td>0,6</td>
<td>0,1</td>
</tr>
<tr>
<td>3</td>
<td>600</td>
<td>4</td>
<td>0</td>
<td>3</td>
<td>0,3</td>
<td>0,6</td>
<td>0,1</td>
</tr>
</tbody>
</table>

Table 3.8 Operating conditions for analyze the effect of pressure

<table>
<thead>
<tr>
<th>Exp</th>
<th>T</th>
<th>Pret</th>
<th>Pperm</th>
<th>u/umf</th>
<th>H2O [mole%]</th>
<th>N2 [mole%]</th>
<th>CH4 [mole%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>500</td>
<td>2</td>
<td>0</td>
<td>3</td>
<td>0,3</td>
<td>0,6</td>
<td>0,1</td>
</tr>
<tr>
<td>2</td>
<td>500</td>
<td>3</td>
<td>0</td>
<td>3</td>
<td>0,3</td>
<td>0,6</td>
<td>0,1</td>
</tr>
<tr>
<td>3</td>
<td>500</td>
<td>4</td>
<td>0</td>
<td>3</td>
<td>0,3</td>
<td>0,6</td>
<td>0,1</td>
</tr>
<tr>
<td>4</td>
<td>500</td>
<td>5</td>
<td>0</td>
<td>3</td>
<td>0,3</td>
<td>0,6</td>
<td>0,1</td>
</tr>
</tbody>
</table>

Table 3.9 Operating conditions for analyze the effect of velocity

<table>
<thead>
<tr>
<th>Exp</th>
<th>T</th>
<th>Pret</th>
<th>Pperm</th>
<th>u/umf</th>
<th>H2O [mole%]</th>
<th>N2 [mole%]</th>
<th>CH4 [mole%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>500</td>
<td>4</td>
<td>0</td>
<td>2,5</td>
<td>0,3</td>
<td>0,6</td>
<td>0,1</td>
</tr>
<tr>
<td>2</td>
<td>500</td>
<td>4</td>
<td>0</td>
<td>3</td>
<td>0,3</td>
<td>0,6</td>
<td>0,1</td>
</tr>
<tr>
<td>3</td>
<td>500</td>
<td>4</td>
<td>0</td>
<td>3,5</td>
<td>0,3</td>
<td>0,6</td>
<td>0,1</td>
</tr>
</tbody>
</table>

The system is initially fed with H2O, N2 and CH4 in order to let happen the steam methane reforming and water gas shift reactions according to equation (1) and (2) while the equilibrium constant are defined with equations (3) and (4).

\[
CH_4 + H_2O \rightarrow CO + 3H_2 \quad (1)
\]

\[
CO + H_2O \rightarrow CO_2 + H_2 \quad (2)
\]
The experiments are taken with a FBR and with a MFBR in which the membrane is a palladium membrane for hydrogen production.

### 3.3.1 Delphi model

The model used is Delphi7, in order to simulate the operation of the reactor from the feeding to the hydrogen production. The main hypothesis of the model are:

- Isothermal conditions was considered because fluidized beds provide uniform temperature over a wide range of superficial gas velocities.
- There are two possible concept to describe the membrane fluidized bed reactor, the first is concept one, the second is concept two. Concept1 is the reactor shows in figure 3.15, in which perovskite membranes are integrated in an oxidation section at the bottom and the Pd membranes at the top.

In the concept 1 a unique design aspect compared to previously proposed reactor concepts is the use of dense perovskite membranes to introduce pure O2 instead of air, with which a large dilution with N2 with a correspondingly large increase in the reactor volume and required H2 membrane surface area can be avoided or, alternatively, the costly cryogenic air separation required for the production of pure O2 can be circumvented. Another important advantage is that, with complete CH4 conversion, pure CO2 is obtained via a simple CO2/steam separation, which avoids CO2 emissions to the atmosphere or an expensive CO2 sequestration. Because metallic membranes for H2 can only be operated at temperatures below 600–700 °C because of membrane stability, while acceptable O2 fluxes through available perovskite O2 membranes can

---

\[ K_{smr} = \exp \left( - \frac{26830}{T} + 30114 \right) \]  
(3)

\[ K_{wgs} = \exp \left( \frac{4400}{T} - 4036 \right) \]  
(4)

---

Figure 3.15 Staged membrane reactor with two modules
only be realized above 900–1000 °C, incorporation of both H2 and O2 membranes inside a single reactor requires purposely created temperature zones in the reactor. A new membrane-assisted fluidised bed reactor is proposed where perovskite membranes are integrated in an oxidation section at the bottom and the Pd membranes in a reforming/shift section at the top.

In the concept 2 described in figure 3.16 hydrogen permselective membranes are integrated in a fluidized bed reactor. In this process, the methane and steam are fed to a fluidized bed reactor, which is operated at high pressure and intermediate temperature depending on the membrane resistance. SMR and WGS reactions occur in a single unit and H2 is formed. The presence of the membranes allows the direct separation of almost pure H2 (according to the selectivity of the membrane adopted) shifting the thermodynamic equilibrium of the reactions towards the products. The heat of reaction is supplied by burning part of the produced H2 which permeates to U-shaped membranes, which are also immersed in the bed. These membranes are fed with air and the H2 combustion provides in-situ the heat needed to achieve auto-thermal operation without external heat exchange. Moreover, the fluidization conditions provide good gas mixing, while a virtually uniform temperature is assured via the internal solids circulation.

![Fluidized bed membrane reactor](image)

Figure 3.16 Fluidized bed membrane reactor

In the model we included SMR and WGS reactions, but not the partial oxidation as before explained. Others important hypothesis are the inclusion of mass transfer and hydrogen membrane, because for the MFBR, the presence of membrane allows direct separation of almost pure hydrogen.

In Delphi there are many procedures which allows to define thermodynamic, kinetic and hydrodynamic conditions. First of all, procedure called “Concept2” defines geometrical parameters such as the membrane hydrogen diameter and membrane length respectively equal to 0,01 m and 0,13 m. The height of the packed bed equal to 0,17 m, the number of CISTR’s emulsion phase equal to 6, the factor of additional CISTR in the gas phase equal to 1, the height of fluidized bed reactor equal to 0,17 and the number of hydrogen membrane that for concept 2 is equal to 1, but if it is changed in 0, we are modelling a normal fluidized bed reactor.
Procedure “ReactorData” describes thermodynamic parameters, such as temperature, pressure and minimum fluidization velocity. In Concept2, temperature of top, bottom and feed is the same because of how the reactor is modelled.

The minimum fluidization velocity is calculated in accordance with Shiau equation:

\[ u_{mf} = \left( \frac{\mu_g}{\rho_g d_p} \right) \left( \sqrt{(27.2)^2 + 0.0408 Ar} - 27.2 \right) \]

Where \( \mu_g \) is the viscosity of the gas, \( \rho_g \) the density of the gas, \( d_p \) the particle diameter and \( Ar \) is the Archimedes number, defined as below:

\[ Ar = \frac{d_p^3 \rho_p (\rho_p - \rho_g)}{\rho_g \mu_g^2} \]

In which \( \rho_p \) is the density of the particle. In this procedure, the inlet composition of the gas is established as input in which it is possible to put the molar flux of hydrogen, methane, oxygen, nitrogen, carbon dioxide, and carbon monoxide.

In the procedure “CalculationReactionKinetic” there are the kinetic parameters as the reactions constant according to equation (1) and (2).

\[ k_2 = 262000 \times \exp \left( -\frac{106900}{R_{gas} \times T} \right) \]  
(1)

\[ k_3 = 245 \times \exp \left( -\frac{54500}{R_{gas} \times T} \right) \]  
(2)

It contains steam methane reforming and water gas shift reactions, with their reaction rate constants, calculated in accordance with Arrhenius equation. Rates of reactions are in accordance with Numaguchi equations (3) and (4) for methane steam reforming and water gas shift on Ni catalyst.

\[ r_2 = \frac{k_2 (p_{CH_4}p_{H_2O} - p_{H_2}^3p_{CO_2}^{1596})}{p_{H_2O}^{1596}} \]  
(3)

\[ r_3 = \frac{k_3 (p_{CO}p_{H_2O} - p_{H_2}^3p_{CO_2})}{p_{H_2O}} \]  
(4)

In the procedure “CalculationHydrogenMembraneFlux” there is mass transport’s equation described in equation (5) and (6) that is defined according to Sieverts-Fick law.

\[ J_{H_2} = \frac{p_{m,pd} n_m}{t_{m,pd}} \left( p_{H_2,f}^{n_m} - p_{H_2,p}^{n_m} \right) \]  
(5)
\[ p_{m,Pd} = p_{m,Pd0} \exp\left(-\frac{E_{act,Pd}}{RT}\right) \] (6)

Where \( p_{m,Pd} \) is the permeability of Pd membrane equal to \( 4,24 \times 10^{-10} \times \exp(-5810/(8,314 \times T)) \), \( t_{m,Pd} \) the Pd membrane thickness equal to \( 5 \times 10^{-6} \), \( p_{H_2,F}^{n_m} \) the partial pressure of H2 on feed side, \( p_{H_2,P}^{n_m} \) the partial pressure of H2 on permeate side, \( p_{m,Pd0} \) the pre-exponential factor for permeability of Pd membrane, while \( E_{act,Pd} \) is the activation energy of Pd membrane. While \( n_m \) is the exponential in the Sievert-Fick law that for this case is equal to 0.74.

Inlet gas composition is measured with Brooks mass flow meters that is a fast instrument but not so accurate. Another interesting instrument that is more accurate is the X-rat photoelectron that is slower but precise.
Chapter 4
Results and considerations:

4.1 Results of collecting particles method

The results for collecting particles in the fuel columns, as well as the standard deviation over the measurements, are shown in table 4.1.1.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Solid Circulation Rates (g/s)</th>
<th>Standard deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Left</td>
<td>Right</td>
</tr>
<tr>
<td>1</td>
<td>22.40</td>
<td>21.90</td>
</tr>
<tr>
<td>2</td>
<td>6.61</td>
<td>5.71</td>
</tr>
<tr>
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<td>25.50</td>
</tr>
<tr>
<td>4</td>
<td>33.00</td>
<td>35.10</td>
</tr>
<tr>
<td>5</td>
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<td>21.13</td>
</tr>
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<td>6</td>
<td>28.35</td>
<td>25.08</td>
</tr>
<tr>
<td>7</td>
<td>20.4</td>
<td>17.79</td>
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<tr>
<td>8</td>
<td>26.99</td>
<td>24.30</td>
</tr>
<tr>
<td>9</td>
<td>8.27</td>
<td>8.02</td>
</tr>
<tr>
<td>10</td>
<td>14.98</td>
<td>13.43</td>
</tr>
<tr>
<td>11</td>
<td>5.99</td>
<td>5.93</td>
</tr>
<tr>
<td>12</td>
<td>8.39</td>
<td>8.36</td>
</tr>
</tbody>
</table>

The first three experiments are taken with different superficial gas velocity in the riser. It is possible to see that when the gas velocity is increased also the solid circulation rate becomes higher as it is shown in figure 4.1. The SCR can be defined according to the equation (1) applied in the riser column, thus when the superficial gas velocity increases, also particle velocity does, which provides an increased amount of solids circulating in the reactor.

$$SCR = u_p \cdot \varepsilon_s \cdot A \cdot \rho_s$$  \hspace{1cm} (1)
The fourth and fifth experiments analyze the influence of the superficial gas velocity in the fuel columns on the solid circulation rates. However, in these cases the difference in the results is not so evident as compared to an increase in the superficial gas velocity in the riser column as depicted in figure 4.2.

**Figure 4.2 Trend of SCR with superficial gas velocity in the fuel columns in the fourth and fifth experiments**
The purpose of the sixth and seventh experiments was to analyze the influence of the solids inventory on the solid circulation rate. The results show that when the solids inventory increases, also the SCR becomes higher due to the increase in the solids holdup (equation 1) as it is shown in figure 4.3.

![Figure 4.3 Trend of SCR with solids inventory for sixth and seventh experiments](image)

In the eighth, ninth and tenth experiments the influence of particle size is analyzed on the solid circulation rates. For these cases it is not possible to use the same ratio between superficial gas velocity and minimum fluidization velocity because the fluidization conditions for the same value of solids inventory are different. It means it is not possible to compare the results of SCR for glass beads of 500 μm and 250 μm. The same trend of SCR is found when the solids inventory is changed, as already described. The solids inventory is a parameter that can influence a lot the SCR.

In the next three experiments the influence of particle type is described using glass beads with 388 μm. This time it is possible to compare the results of SCR between the new particles and the glass beads with 500 μm of mean diameter since the ratio between the superficial gas velocity and the minimum fluidization velocity is the same in the first and eleventh experiment. The comparison between these cases shows the SCR is hardly influenced by particle size as it is possible to see in table 4.2.

**Table 4.2 SCR and operative conditions in experiment 1 and 11**

<table>
<thead>
<tr>
<th>Exp</th>
<th>d_p [μm]</th>
<th>u/umf riser</th>
<th>u/umf fuel</th>
<th>solids inventory [kg]</th>
<th>SCR</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>500</td>
<td>15</td>
<td>1.66</td>
<td>2</td>
<td>22.4</td>
</tr>
<tr>
<td>11</td>
<td>388</td>
<td>15</td>
<td>1.66</td>
<td>2</td>
<td>20.4</td>
</tr>
</tbody>
</table>
The effect of sphericity on SCR is also studied in the other experiments as sand particles with a sphericity of 0.75 are used in this work. Particle size and density of sand are close to glass beads, which means that the only real parameter that is analyzed is the change in sphericity.

The sphericity is measured using a Cilas machine that analyzes the images of particles to give different parameters: aspect ratio, circularity and sphericity.

The aspect ratio measures the ratio of the particle height to its width, which can be defined according to equation (2).

\[ A_R = \frac{\text{minFeretDiameter}}{\text{maxFeretDiameter}} \] (2)

Where the \text{minFeretDiameter} is the smallest distance between two tangents on opposite sides of the particle parallel to some fixed directions as it is described in figure 4.4 (number 4) and the \text{maxFeretDiameter} is the largest distance between two tangents on opposite sides of the particle parallel to some fixed directions as it is described in figure 4.4 (number 3).

![Figure 4.4 MinFeretDiameter and MaxFeretDiameter](image)

The circularity ratio is defined as the ratio of the area of the shape to the area of a circle having the same perimeter, which is defined as stated in equation (3).

\[ f_{\text{circ}} = 4\pi \frac{A}{P^2} \] (3)

The closer the shape of a particle is to a disk, the closer the circularity ratio is to 1.

Sphericity is defined as the Inscribing disk divided by the Circumscribing disk according to the equation (4). The inscribing disk radius is the smallest distance between the contour and the center of gravity. The
circumscribing disk radius is the largest distance between the contour and the center of gravity as it is possible to see in figure 4.5.

![Figure 4.5 Description of sphericity with Cilas machine](image)

\[ sphericity = \frac{R_{\text{circumscribing}}}{R_{\text{inscribing}}} \]  (4)

The parameter that can describe better the real 3D sphericity using 2D images is the aspect ratio and for all the experiments done with non-spherical particles, the sphericity is measured according with the aspect ratio.

The solid circulation rates measured for sand with a ratio between the superficial gas velocity and minimum fluidization velocity equal to 14 is really different compared to the other cases in which the ratio is 15. It means the sphericity is a really important parameter that can influence a lot the result of SCR, especially the minimum fluidization velocity. When umf is decreased, the total amount of gas fed to keep a similar ration between superficial gas velocity and minimum fluidization conditions is clearly decreased. This implies that the particle velocity will be decreased in the riser column, thus reducing the extent of solids transferred to the side columns. The solid circulation rate for sand is lower compared to the other case because the friction effect become really important for non spherical particles as the drag coefficient has a different trend for spherical and non particles as it is possible to see in figure 4.6 according to Haider and Levenspiel [3].

The drag force reduces the velocity of particles immersed in the fluid, so it could explain why the solid circulation rate decreases when the particles are not spherical.

In this work also activated alumina particles has been used to study the effect of particle density for a reasonably similar sphericity compared to sand. The sphericity is measured again with the Cilas machine giving a value of 0.776. As already said the SCR is lower for alumina because they are non-spherical particles. However the solid circulation rate for activated alumina is lower compared to sand because the other important parameter affecting the system is the density. In the table 4.3 it is possible to see the comparison between the first case of sand and the second case of activated alumina, in which all the operative conditions are the same except for density and sphericity. Since the sphericity is higher in activated alumina than in sand, it means the SCR should be higher for alumina but it is not in this way. The explanation is found in the fact that the voids of a particle is really higher in alumina than in sand so the main different is the density: 2600 kg/m³ for sand instead of 1135
kg/m³ for activated alumina. In the experiments with activated alumina, the solids inventory is 1.3 kg while for sand is 2 kg because since the density is different, also the solids inventory in order to have the same height of particles in the reactor is not the same. In this case, again the main parameter affecting the results is the decrease in minimum fluidization velocity, which directly implies a decrease in the superficial gas velocity fed to carry along the particles.

![Drag laws of Ganser and Haider and Levenspiel depending on the sphericity](image)

Figure 4.6 Drag laws of Ganser and Haider and Levenspiel depending on the sphericity

<table>
<thead>
<tr>
<th>Exp</th>
<th>d_p[μm]</th>
<th>u/umf riser</th>
<th>u/umf fuel</th>
<th>solids inventory [kg]</th>
<th>SCR</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>460</td>
<td>14</td>
<td>1,35</td>
<td>2</td>
<td>8,27</td>
</tr>
<tr>
<td>18</td>
<td>510</td>
<td>14</td>
<td>1,4</td>
<td>1,3</td>
<td>6,65</td>
</tr>
</tbody>
</table>

Table 4.3 Comparison between SCR and operative conditions in experiment 14 and 18

It is possible to conclude that the main parameters affecting the solid circulation rates are the velocity in the riser, the amount of particle, the density and the sphericity.
4.2 Results with PIV-DIA method

The PIV-DIA results show that it is possible to correlate the measured 2D intensities to 3D porosities by using a linear correlation. This is possible as the extent of solids holdup is much less as compared to the use of fluidized beds. Results obtained using this novel optical technique are presented in table 4.3.

\[ \varepsilon_{3D} = A \times \varepsilon_{2D} \quad (5) \]

Figure 4.7 Correlation 2D-3D porosity in the fuel reactors

For the same A, the porosity 2D could be connected to porosity 3D, giving a value of solid circulation rate near to the collecting particles.

Table 4.4 contains the results for optical technique without the background correction and it is possible to see that especially in the sixth and seventh experiments, the left and right column are influenced from different illumination since the value of solid circulation rate is quite different.

Table 4.4 shows also the results for PIV-DIA method with the fixed background correction and it is possible to see that the results in the left and right columns are closer compared to the case without background correction.

All the consideration related to the solid circulation rates and the parameters that can affect it are the same as described before. For both the case with and without background, the value of A is equal to 0.049 obtained fitting the first seven experiments in order to minimize the absolute deviation to collecting particles. The maximum error in the case of background correction is equal to 20.1 % while for the method without background correction the absolute deviation is equal to 33%. 
Table 4.4 Results of SCR for optical technique without and with background correction and their deviation to collecting particles method

<table>
<thead>
<tr>
<th>Exp</th>
<th>Solid Circulation Rates (g/s) without background correction</th>
<th>Deviation to collected particles (%)</th>
<th>Solid Circulation Rates (g/s) with background correction</th>
<th>Deviation to collected particles (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Left</td>
<td>Right</td>
<td>Left</td>
<td>Right</td>
</tr>
<tr>
<td>1</td>
<td>25.8</td>
<td>20.8</td>
<td>15.18</td>
<td>5.02</td>
</tr>
<tr>
<td>2</td>
<td>34</td>
<td>28.7</td>
<td>2.58</td>
<td>10.59</td>
</tr>
<tr>
<td>3</td>
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<td>6.7</td>
<td>1.36</td>
<td>17.34</td>
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<tr>
<td>4</td>
<td>17.5</td>
<td>17.5</td>
<td>9.89</td>
<td>9.23</td>
</tr>
<tr>
<td>5</td>
<td>22.4</td>
<td>22.1</td>
<td>10.83</td>
<td>13.33</td>
</tr>
<tr>
<td>6</td>
<td>29.1</td>
<td>21.5</td>
<td>22.58</td>
<td>20.07</td>
</tr>
<tr>
<td>7</td>
<td>36.9</td>
<td>26.8</td>
<td>11.82</td>
<td>23.65</td>
</tr>
<tr>
<td>8</td>
<td>24.6</td>
<td>19.2</td>
<td>22.21</td>
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</tr>
<tr>
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<td>25.3</td>
<td>21.4</td>
<td>8.63</td>
<td>9.09</td>
</tr>
<tr>
<td>10</td>
<td>27.6</td>
<td>23.1</td>
<td>2.65</td>
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</tr>
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<td>35.5</td>
<td>0.64</td>
<td>10.48</td>
</tr>
<tr>
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<td>9.8</td>
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<td>18.5</td>
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</tr>
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<td>13.2</td>
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<tr>
<td>16</td>
<td>17.7</td>
<td>14.9</td>
<td>15.18</td>
<td>5.02</td>
</tr>
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<td>6.8</td>
<td>7.9</td>
<td>13.43</td>
<td>33.1</td>
</tr>
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<td>6.2</td>
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<td>6.76</td>
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</tr>
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<td>19</td>
<td>9.4</td>
<td>9.9</td>
<td>12.09</td>
<td>18.4</td>
</tr>
</tbody>
</table>

The PIV-DIA method allows the measurement of the 3D solids holdup using the linear correlation already explained. In the table 4.5 the solids holdup in the fuel columns are shown.

The first important consideration is related to the fact that the system is very diluted and the solids holdup are in agreement with the values that is possible to find in the literature for similar systems.

A second important consideration consists in the parameters that are affecting the solids holdup. As already said the solids inventory influence the solids holdup because if the solids holdup is defined according to the equation (6), it means the voids of the bed decrease when the solids inventory increases.

\[ \varepsilon_S = (1 - \varepsilon_B) \ast (1 - \varepsilon_P) \]  

(6)

Where \( \varepsilon_S \) is the solids holdup, \( \varepsilon_B \) represent the voids of the bed while \( \varepsilon_P \) is the voids of a particle.
When the velocity in the riser is increased, the solids holdup in the fuel columns become higher as it is possible to see in the figure 4.8. The explanation could be found on the fact that when the superficial gas velocity in the riser is increased, it means more particles are going out from the center to the fuel reactors in order to have a lot of particles in the external vessels, so the parameter $1 - \varepsilon_B$ increases and the solids holdup becomes higher.

**Table 4.5 Description of solids holdup in the left and right columns**

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Solid Circulation Rates (g/s)</th>
<th>Solids holdup</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Left</td>
<td>Right</td>
</tr>
<tr>
<td>1</td>
<td>22.4</td>
<td>21.9</td>
</tr>
<tr>
<td>2</td>
<td>34.9</td>
<td>32.1</td>
</tr>
<tr>
<td>3</td>
<td>6.61</td>
<td>5.71</td>
</tr>
<tr>
<td>4</td>
<td>19.42</td>
<td>19.28</td>
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<tr>
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<td>25.12</td>
<td>25.5</td>
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<td>35.1</td>
</tr>
<tr>
<td>8</td>
<td>20.13</td>
<td>21.13</td>
</tr>
<tr>
<td>9</td>
<td>23.9</td>
<td>23.54</td>
</tr>
<tr>
<td>10</td>
<td>28.35</td>
<td>25.08</td>
</tr>
<tr>
<td>11</td>
<td>20.4</td>
<td>17.79</td>
</tr>
<tr>
<td>12</td>
<td>26.99</td>
<td>24.3</td>
</tr>
<tr>
<td>13</td>
<td>34.12</td>
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<td>8.02</td>
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<td>6.47</td>
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<tr>
<td>19</td>
<td>8.39</td>
<td>8.36</td>
</tr>
</tbody>
</table>

**Figure 4.8 Trend of solids holdup with velocity in the riser**
The figure 4.9 describes the correlation between solids holdup and solids inventory. When the amount of particles is increased, the voids of the bed decreases and again the parameter \((1 - \varepsilon_B)\) becomes higher.

To use of PIV-DIA in the riser becomes more difficult since its hydrodynamics behavior is more turbulent as compared to the one observed in the fuel columns. In this case, the background method selected for this column consists in a dynamic image generated from all the individual images obtained during the recording of the experiments. In this column the same linear correlation found in the fuel columns is still applicable and the value of A that can minimize the absolute deviation is equal to 0.032. The results are shown in table 4.6.
Table 4.6 SCR with optical techniques in the riser

<table>
<thead>
<tr>
<th>Experiment</th>
<th>SCR for PIV-DIA [g/s]</th>
<th>Standard deviation to collecting method [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Riser</td>
<td>Riser</td>
</tr>
<tr>
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<td>39.5</td>
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</tr>
<tr>
<td>2</td>
<td>56.2</td>
<td>21.23</td>
</tr>
<tr>
<td>3</td>
<td>13.5</td>
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<td>12.87</td>
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<td>16.87</td>
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<td>18.43</td>
</tr>
<tr>
<td>17</td>
<td>12.5</td>
<td>4.79</td>
</tr>
<tr>
<td>18</td>
<td>14.3</td>
<td>9.03</td>
</tr>
<tr>
<td>19</td>
<td>18.5</td>
<td>10.47</td>
</tr>
</tbody>
</table>

In this column, the SCR measured experimentally represent the sum of the SCR measured in the left and right fuel columns. The main parameters affecting the SCR are velocity in the riser, solids inventory, density and sphericity, and a maximum absolute deviation for optical technique in the riser is equal to 21.23 %. The fact that the value of A is different for external vessels and the riser depends on the different background correction used.

4.3 Results with pressure transducer method

The measurement of pressure drop in the riser allows to measure the solid circulation rate in the air reactor. The figure 4.10 describes the pressure trend along the height of the riser column. The transducer located at the bottom is characterized from the higher pressure according to the Stevin’s law for which the pressure increases when the height decreases.
The pressure transducer method based on the Bernoulli and Richardson and Zaki equations is able to give the mean solids holdup in the riser and the average particle velocity in order to find the solid circulation rate. The Figure 4.11 represents the solids holdup profile with the height. These values are found by applying the pressure method between two consecutive pressure transducers and the successively from the bottom to the top of the riser column. The trend could be explained considering the fact that at the top of the reactor, the solids holdup is lower because there are only the particles going out from the riser to the fuel reactors while the bottom part behaves more as a expanded bed in which the void fraction is reduced and the solids holdup becomes higher.

The table 4.7 contains the results of SCR with pressure transducer method. An important consideration is related to the fact that the maximum absolute deviation to the collecting method is 23.18% while for most of
the cases the deviation is lower than 10%. It means the new method is accurate to describe the solid circulation rate of the system.

The behavior of solids holdup in the riser is quite different compared to the one in the fuel columns because as already said the system is systematically different and the change of pressure drop is connected to this different conduct.

Table 4.7 Results of SCR with pressure transducers technique

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Collecting particles (g/s)</th>
<th>SCR with pressure sensors</th>
<th>Error (%)</th>
<th>Solids holdup</th>
</tr>
</thead>
<tbody>
<tr>
<td>Center</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>44.3</td>
<td>47.31</td>
<td>6.79</td>
<td>0.023</td>
</tr>
<tr>
<td>2</td>
<td>67.00</td>
<td>55.28</td>
<td>17.48</td>
<td>0.014</td>
</tr>
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<td>12.32</td>
<td>15.18</td>
<td>23.18</td>
<td>0.035</td>
</tr>
<tr>
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<td>40.09</td>
<td>3.59</td>
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</tr>
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<td>50.62</td>
<td>47.37</td>
<td>6.42</td>
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</tr>
<tr>
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<td>50.64</td>
<td>51.42</td>
<td>1.53</td>
<td>0.027</td>
</tr>
<tr>
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<td>68.19</td>
<td>63.65</td>
<td>6.53</td>
<td>0.032</td>
</tr>
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<td>41.26</td>
<td>44.00</td>
<td>6.64</td>
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<tr>
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</tr>
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<td>37.05</td>
<td>3.00</td>
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<td>51.29</td>
<td>47.96</td>
<td>6.5</td>
<td>0.036</td>
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<td>14</td>
<td>19.00</td>
<td>16.58</td>
<td>1.78</td>
<td>0.023</td>
</tr>
<tr>
<td>15</td>
<td>25.9</td>
<td>26.19</td>
<td>3.93</td>
<td>0.014</td>
</tr>
<tr>
<td>16</td>
<td>32.6</td>
<td>31.63</td>
<td>12.16</td>
<td>0.035</td>
</tr>
<tr>
<td>17</td>
<td>14.7</td>
<td>12.93</td>
<td>8.4</td>
<td>0.022</td>
</tr>
<tr>
<td>18</td>
<td>13.7</td>
<td>14.11</td>
<td>7.58</td>
<td>0.023</td>
</tr>
<tr>
<td>19</td>
<td>19.3</td>
<td>17.63</td>
<td>5.3</td>
<td>0.028</td>
</tr>
</tbody>
</table>

For the first three experiments, in which the gas velocity in the riser is changed, the solids holdups do not follow the principle of proportionality as said for the fuel reactors but when the velocity increases, the solids holdup becomes lower as it is described in figure 4.12.
As the same time it is possible to see that the pressure drop decreases when the superficial gas velocity increases, as it is possible to see in figure 4.13.

The explanation for these trends of pressure drop and solids holdup can be found considering that when the superficial gas velocity is increased in the riser there are more particles going out from the riser to the fuel reactors and it means the solids holdup decreases. The pressure drop deeply depends on the weight of particles in the reactor so if the solids holdup is lower when the velocity increases, it means also the pressure drop should be lower.

In the sixth and seventh experiments in which the solids inventory is increased, the solids holdup and the pressure drop become higher because the amount of particles in the riser is more as described in figure 4.14.
In the experiments with glass beads with a mean diameter of 250 μm the solids holdup and the pressure drop become the highest of all the cases because if the particle size is lower, it means the voids of the bed decrease and the solids holdup is higher. In the cases of 388 μm the solids holdup and pressure drop are higher than the case of 500 μm but lower than the case of 250 μm as it is possible to see in figure 4.15.

The pressure transducer method for sand and activated alumina is less accurate because the fluctuation of pressure drop is quite high as every particle has different sphericity. As already said the sphericity influences the terminal velocity and thus the solid circulation rate. It means that if the particles do not have exactly the same sphericity, but there is a little different from one to another, the velocity with which they reach the top of the riser is different and the pressure fluctuation increases. Looking to the deviation for the pressure transducers method, it is possible to see it is really accurate for all the experiments expect for sand and activated alumina, as it is represent in figures 4.16 and 4.17.
The absolute deviation in figure 4.16 is found considering the pressure fluctuation respect to the average plus minus the standard deviation. The maximum deviation is around 5 g/s that is the 10% of the SCR.

However, related to the solids holdup for activated alumina and since the bulk density is quite low compared to the other cases and the voids of a particle are really high, it means in the equation (6) the parameter $1 - \varepsilon_p$ is low and the total $\varepsilon_S$ become lower compared to the fourth experiments in which except for sphericity and density, the operative conditions are similar.

Furthermore, average solids hold-up in the riser can be measured using the pressure drop method between two positions in the riser. The optical technique also allows to measure porosities in the riser after background correction and both can be compared. As summarized in table 4.7 there is also a good agreement in terms of solids hold-up when using the two different methods. Furthermore, these values are in good agreement with typical measured hold-up values presented in the literature.
Table 4.7 Average solids hold-up measured in the riser column using the PIV/DIA and the pressure drop methods for all the experiments in this work

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>PIV/DIA method</th>
<th>Pressure drop method</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0247</td>
<td>0.0227</td>
</tr>
<tr>
<td>2</td>
<td>0.0187</td>
<td>0.014</td>
</tr>
<tr>
<td>3</td>
<td>0.0279</td>
<td>0.0354</td>
</tr>
<tr>
<td>4</td>
<td>0.0239</td>
<td>0.0214</td>
</tr>
<tr>
<td>5</td>
<td>0.0259</td>
<td>0.0252</td>
</tr>
<tr>
<td>6</td>
<td>0.0257</td>
<td>0.0266</td>
</tr>
<tr>
<td>7</td>
<td>0.0272</td>
<td>0.0303</td>
</tr>
<tr>
<td>8</td>
<td>0.0581</td>
<td>0.051</td>
</tr>
<tr>
<td>9</td>
<td>0.0622</td>
<td>0.055</td>
</tr>
<tr>
<td>10</td>
<td>0.0634</td>
<td>0.056</td>
</tr>
<tr>
<td>11</td>
<td>0.0382</td>
<td>0.0405</td>
</tr>
<tr>
<td>12</td>
<td>0.0340</td>
<td>0.0360</td>
</tr>
<tr>
<td>13</td>
<td>0.0283</td>
<td>0.0325</td>
</tr>
<tr>
<td>14</td>
<td>0.0247</td>
<td>0.0227</td>
</tr>
<tr>
<td>15</td>
<td>0.0187</td>
<td>0.0140</td>
</tr>
<tr>
<td>16</td>
<td>0.0279</td>
<td>0.0354</td>
</tr>
<tr>
<td>17</td>
<td>0.0253</td>
<td>0.0224</td>
</tr>
<tr>
<td>18</td>
<td>0.0257</td>
<td>0.0231</td>
</tr>
<tr>
<td>19</td>
<td>0.0321</td>
<td>0.0284</td>
</tr>
</tbody>
</table>

Figure 4.17 shows the solid fluxes as a function of the lateral position at an axial position which corresponds to the middle of the window selected for the optical technique. In this figure the solid fluxes at that corresponding height are compared for the three first experiments. As expected, it is observed that the experiment with the highest SCR (experiment 2) of this set of three experiments leads to higher areas behind the curves. Furthermore, it is also observed that the sum of all negative solid fluxes corresponding to the fuel columns is compensated by the sum of all positive fluxes measured in the riser column, which is related to SCR mass balance in these types of reactors.
A parity plot with the comparison of the three methods is depicted in figure 4.19. From this figure it is observed that a narrow deviation over the measured SCR by collecting particles is obtained by the other two novel methods, hence implying a good accuracy for the prediction of SCR.
Figure 4.19 Parity plot for SCR measured using PIV/DIA and pressure drop methods compared to SCR determined experimentally by collecting particles and their deviation. Dashed lines represent the deviations in the measurements.
Chapter 5
Results and considerations of MFBR

5.1 Experiments

In the new hybrid concept fuel conversion takes place in the fuel reactor, which is a fluidized bed membrane reactor. In this case, it becomes important to predict the behavior of the fuel reactor through phenomenological models and comparison to experiments. The knowledge gained during the measurements on SCR in the interconnected reactor might be implemented in phenomenological models for interconnected fluidized beds operating at different conditions. In this chapter the potential of fuel conversion in a fluidized bed membrane reactor using metallic supported membranes is analyzed by studying the influence of different operating conditions (viz. temperature, pressure and superficial gas velocity).

The phenomenological model is based on solving hydrodynamics and mass balances accounting for reaction kinetics. The kinetic expression for the fuel reactor is based on Numaguchi and Kikuchi [5]. Information on the model can be found elsewhere [reference]. For the comparison of the results, the two main reactions (SMR and WGS) are considered (1) and (2).

\[
\begin{align*}
CH_4 + H_2O & \rightarrow CO + 3H_2 \quad (1) \\
CO + H_2O & \rightarrow CO_2 + H_2 \quad (2)
\end{align*}
\]

The main parameter for the comparison of experimental results and modelling is the methane conversion, which is defined according to equation (3).

\[
CH_4 \text{ conversion} = \frac{(CH_4 \text{ inlet} - CH_4 \text{ outlet})}{CH_4 \text{ inlet}} \quad (3)
\]

The hydrogen selectivity is used to understand how much methane produces hydrogen and it is described in the equation (4).

\[
H_2 \text{ selectivity} = \frac{H_2 \text{ retentate}}{4 \times (CH_4 \text{ inlet} - CH_4 \text{ outlet})} \quad (4)
\]

The hydrogen recovery and separation factors are defined respectively according to equation (5) and (6).

\[
\text{Hydrogen recovery factor} = \frac{H_2 \text{ permeate}}{4 \times CH_4 \text{ inlet}} \quad (5)
\]
\[ \text{Separation factor} = \frac{H_2 \text{ permeate}}{H_2 \text{ permeate} + H_2 \text{ retentate}} \quad (6) \]

5.2 Results for the effect of temperature

First of all, the effect of temperature is analyzed, so the Table 5.1 shows the results of modelling and experiments for FBR.

Table 5.1 Results of modelling and experiments for FBR changing the temperature conditions

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>CH4 inlet [ml/min]</th>
<th>Pressure [bar]</th>
<th>CH4 conversion experimental</th>
<th>CH4 conversion modelling</th>
</tr>
</thead>
<tbody>
<tr>
<td>786.45</td>
<td>420</td>
<td>4.06</td>
<td>0.3829</td>
<td>0.3896</td>
</tr>
<tr>
<td>820.85</td>
<td>420</td>
<td>3.93</td>
<td>0.4834</td>
<td>0.4920</td>
</tr>
<tr>
<td>872.85</td>
<td>420</td>
<td>3.98</td>
<td>0.6367</td>
<td>0.6504</td>
</tr>
</tbody>
</table>

The most important remark is related to the fact that when the temperature increases, also the methane conversion raises as the overall system is endothermic. The values of methane conversion from model and experiments are almost the same but the little difference could be explained considering the possible difference in the choice of parameters, from model to experiments.

The effect of temperature is subsequently analyzed in the fluidized bed membrane reactor configuration. The Table 5.2 describes the results for experimental and modelling part.

Table 5.2 Results of model and experiments for MFBR changing the temperature conditions

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>799.4</td>
<td>420</td>
<td>4.2</td>
<td>0.5194</td>
<td>0.4821</td>
<td>0.2497</td>
<td>0.1786</td>
<td>0.4967</td>
<td>0.339</td>
</tr>
<tr>
<td>819.95</td>
<td>420</td>
<td>3.94</td>
<td>0.6751</td>
<td>0.6121</td>
<td>0.3231</td>
<td>0.2202</td>
<td>0.5023</td>
<td>0.339</td>
</tr>
<tr>
<td>870.75</td>
<td>420</td>
<td>4.04</td>
<td>0.841</td>
<td>0.7509</td>
<td>0.4165</td>
<td>0.2619</td>
<td>0.5326</td>
<td>0.337</td>
</tr>
</tbody>
</table>

The increase in temperature causes an increase in the methane conversion in both FBR and MFBR, but as expected, the methane conversion is higher in MFBR due to the displacement of the equilibrium towards products. Fluidized beds provide virtually uniform temperature over a wide range of superficial gas velocities as address by Adris [4], who observed that at a gas velocity of about five times the minimum fluidization velocity the catalyst bed temperature becomes fairly uniform. A membrane surface immersed in a fluidized
bed operated above this velocity experiences virtually isothermal operation. The permeation process is highly temperature dependent, with the permeation rate constant following Arrhenius behavior. Therefore, higher operating temperatures should lead to a higher permeation rate. On the other hand, too high temperatures might compromise the membrane life. For practical cases there should be an optimum operating temperature that gives a desirable permeation rate without compromising the life of membrane. The optimum temperature is determined by the economics of the membrane installation and is different for each application depending on the type of reaction, its kinetic and the permeation capacity requirement.

In the case of FBMR the methane conversion is improved by the hydrogen separation as it is described in figure 5.1.

Methane conversion gives information about the global process and the performance of the catalyst while hydrogen recovery factor and separation factor are associated to the performance of the membrane. Membrane with high permeances will give higher hydrogen recovery factor. Separation factor gives information on the amount of hydrogen permeated from the total amount of hydrogen produced. In membrane technology the permeate refers to the amount of hydrogen that passes through the membrane, while the retentate side refers to the one that does not pass through. The difference observed in methane conversion between the model and experiments might be related to the hydrodynamics of the bed and the real distance from the top end of the membrane and the freeboard of the bed. Anyway in the model, the hydrogen permeate is more than in experiments, indeed the hydrogen recovery factor and the separation factor are greater.

![Figure 5.1 Comparison between FBR and MFBR results from model and experiments](image)

When the temperature raises, as already said, the methane conversion increases, which means there is more methane converted in hydrogen so in the MFBR, more hydrogen crosses the membrane and the hydrogen recovery factor increases. At the same time, since the hydrogen permeate is higher, also the separation factor raises as it is possible to see in figure 5.2. Thermodynamic equilibrium is measured through Aspen considering the equations (7) and (8) characteristic of chemical equilibrium of a reaction.
\[ n_i = n_i^0 + \sum_{j=1}^{NR} n_{ij} \lambda \]  
(7)

\[ \Delta G = \Delta G_R^0 + RT \ln \prod a_i^{\nu_i} \]  
(8)

But since at the equilibrium \( \Delta G \) is equal to 0, it means the equation (8) becomes (9) and (11).

\[ \Delta G_R^0 = -RT \ln \prod a_i^{\nu_i} \]  
(9)

\[ K_{eq} = \prod a_i^{\nu_i} \]  
(10)

\[ \Delta G_R^0 = -RT \ln K_{eq} \]  
(11)

Where \( n_i \) and \( n_i^0 \) are the final and initial number of moles in the reactions, \( \nu_i \) is the stoichiometric numbers, \( \lambda \) is the exent of reaction, \( a \) is the fugacity, \( \Delta G_R^0 \) is the free energy of reaction, \( \Delta G \) is the Gibbs energy and \( K_{eq} \) is the equilibrium constant of reaction. The equilibrium is calculated for the case of fluidized bed reactor and it is composed of maximum points that cannot be reached for FBR in experiments and modelling. In membrane fluidized bed reactor, since the hydrogen is removed, it is possible to work above that thermodynamic equilibrium.

\[ \text{Figure 5.2 Separation and hydrogen recovery factor with temperature} \]

The hydrogen recovery factor increases in an important way, from 0.24 until 0.41 because the methane conversion and hydrogen production are really dependent on the temperature, so a small deviation of
temperature can change a lot the results. It is important in a hydrogen production system to optimize the temperature considering the relevant influence it has.

### 5.3 Results for the effect of pressure

The table 5.3 shows the results of model and experiments in a FBR for the effect of pressure.

**Table 5.3 Results of model and experiments for FBR changing the pressure conditions**

<table>
<thead>
<tr>
<th>Pressure [bar]</th>
<th>CH4 inlet [ml/min]</th>
<th>Temperature [K]</th>
<th>Experimental CH4 Conversion</th>
<th>Modelling CH4 conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.05</td>
<td>420</td>
<td>786.45</td>
<td>0.4899</td>
<td>0.4776</td>
</tr>
<tr>
<td>3.03</td>
<td>420</td>
<td>786.45</td>
<td>0.4292</td>
<td>0.4272</td>
</tr>
<tr>
<td>4.06</td>
<td>420</td>
<td>786.45</td>
<td>0.3829</td>
<td>0.3897</td>
</tr>
<tr>
<td>4.97</td>
<td>420</td>
<td>788.25</td>
<td>0.3653</td>
<td>0.3690</td>
</tr>
</tbody>
</table>

When the pressure increases, the methane conversion decreases in accordance with the equation (12) that describes Le Chatelier’s principle:

\[
Keq = \prod \pi^N \pi^P
\]  

Where \( Keq \) is the equilibrium constant of reaction and at the equilibrium, \( Keq \) is constant, so if the reaction goes in the direction of increasing the moles, when the pressure increases, the equilibrium is shifted to the reactants, and it explains why the methane conversion is reduced. But for the case of membrane fluidized bed reactor, the increase of pressure causes two opposing effects. One is the negative effect given by Le Chatelier’s principle and the other positive is in accordance with mass transfer through the membrane in equation (13).

\[
J_{H2} = \frac{P_m}{\sigma} * (P_R^n - P_P^n)
\]

Where \( J_{H2} \) is the hydrogen flux passed through the membrane, \( P_R^n \) and \( P_P^n \) are respectively the hydrogen partial pressure in retentate and in permeate, \( \sigma \) is the thickness of membrane, while \( P_m \) is the hydrogen permeability defined according to equation (14).

\[
P_m = P_m^0 * \exp \left( -\frac{E_a}{RT} \right)
\]

Where \( P_m^0 \) is the pre-exponential factor and \( E_a \) the activation energy for permeation. The permeation conditions affect the hydrogen flux, so if the pressure increases also hydrogen flux has to increase.

In general if the pressure is increased, the methane conversion decreases but for the case of MFBR since there are two opposites effect, when the pressure is increased, the reduction in methane conversion is less compared to FBR in which there is only the negative effect due to Le Chatelier principle. As results of the two opposite effects, the grade of a line that connect all the points for FBR is more pendent than the line for MFBR. It means that the methane conversion decrease more in FBR than in MFBR for the same increase of pressure as it is possible to see in table 5.4. It is really important to take into consideration that the most
important processes involving hydrogen, use pressurized hydrogen so it is better to work with high pressure even if the methane conversion decreases but the compression costs are saved.

### Table 5.4 Results of model and experiments for MFBR changing the pressure conditions

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>2.05</td>
<td>420</td>
<td>784.05</td>
<td>0.5521</td>
<td>0.549</td>
<td>0.1458</td>
<td>0.3213</td>
<td>0.2459</td>
<td>0.3213</td>
</tr>
<tr>
<td>3.03</td>
<td>420</td>
<td>782.05</td>
<td>0.5104</td>
<td>0.5315</td>
<td>0.1667</td>
<td>0.4171</td>
<td>0.3019</td>
<td>0.4171</td>
</tr>
<tr>
<td>4.06</td>
<td>420</td>
<td>779.45</td>
<td>0.4821</td>
<td>0.5198</td>
<td>0.1786</td>
<td>0.4967</td>
<td>0.3390</td>
<td>0.4967</td>
</tr>
<tr>
<td>4.97</td>
<td>420</td>
<td>763.05</td>
<td>0.4702</td>
<td>0.4969</td>
<td>0.1815</td>
<td>0.5338</td>
<td>0.3556</td>
<td>0.5338</td>
</tr>
</tbody>
</table>

Results are more similar to them, so the experiments worked in a good way for the case of pressure’s effect. The steam methane reforming in a plant is usually carried out at 20-30 bar instead of 1 bar even if the methane conversion decreases, because the refinery need at higher pressure and temperature while the compression cost are higher than working with a lower methane conversion. The figure 5.3 compares what happens if the pressure is changed in MFBR and FBR for modelling and experiments.

It is interesting to observe that the influence of pressure is less relevant for methane conversion than the influence of temperature. The relevant aspect of pressure is the relation with the hydrogen flux that was explained in equation (8).

![Figure 5.3 Comparison between FBR and MFBR with model and experiments changing pressure conditions](image)

As occurring before, in the MFBR configuration there is a difference between model and experiments related to the hydrodynamics of the bed.
When the methane conversion decreases, it means the difference between the inlet methane and the outlet methane is low so only few moles of methane are converted into hydrogen while there is a huge quantity that is not used. With the results of temperature effect it is possible to see that there is a positive trend between the methane conversion and the hydrogen recovery factor and separation factor but it is not the same for the case of pressure effect. Even if the methane conversion decrease and it means the outlet methane is near to the inlet methane, but since the pressure is increased, the hydrogen permeate increase and also the hydrogen recovery factor and separation factor raise, as it is possible to see in figure 5.4.
5.4 Results for the effect of composition

In this test, the steam to carbon ratio is changed from 2 to 4 and the results are described in table 5.5 for FBR with model and experiments.

Table 5.5 Results of model and experiments for FBR changing the composition

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.4</td>
<td>0.1</td>
<td>0.5</td>
<td>4.08</td>
<td>784.25</td>
<td>0.4443</td>
<td>0.4241</td>
</tr>
<tr>
<td>3</td>
<td>0.3</td>
<td>0.1</td>
<td>0.6</td>
<td>4.06</td>
<td>786.45</td>
<td>0.3829</td>
<td>0.3896</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>0.1</td>
<td>0.7</td>
<td>4.03</td>
<td>789.05</td>
<td>0.3231</td>
<td>0.3399</td>
</tr>
</tbody>
</table>

Table 5.6 Results of model and experiments for MFBR changing the composition

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.39</td>
<td>0.09</td>
<td>0.52</td>
<td>4.19</td>
<td>779.46</td>
<td>0.5459</td>
<td>0.5536</td>
<td>0.4755</td>
<td>0.3357</td>
<td>0.2555</td>
<td>0.1964</td>
</tr>
<tr>
<td>3</td>
<td>0.29</td>
<td>0.096</td>
<td>0.614</td>
<td>4.20</td>
<td>779.45</td>
<td>0.5198</td>
<td>0.4821</td>
<td>0.4966</td>
<td>0.339</td>
<td>0.2497</td>
<td>0.1786</td>
</tr>
<tr>
<td>2</td>
<td>0.19</td>
<td>0.100</td>
<td>0.710</td>
<td>4.18</td>
<td>779.95</td>
<td>0.4598</td>
<td>0.4077</td>
<td>0.5124</td>
<td>0.3508</td>
<td>0.2257</td>
<td>0.1548</td>
</tr>
</tbody>
</table>

When the steam to carbon ratio is increased, the conversion also becomes greater since the equilibrium is shifted on the right due to the presence of more reactants. The table 5.6 shows results by experiments and modelling for the case of membrane fluidized bed reactor while figure 5.6 describes the total results for the effect of composition. Steam to carbon ratio is another parameter that can influence the methane conversion but as already said for pressure, it cannot affect the results in a so important way as temperature could.

![Figure 5.6 Comparison between FBR and MFBR with model and experiments changing the composition](image-url)

The hydrogen recovery factor increases with the steam to carbon ratio, since as already said the equilibrium is shifted to the product due to the presence of more reactants. It means more hydrogen is produced and
the hydrogen recovery factor is enhanced. The separation factor that gives information on the amount of hydrogen permeated decreases with the steam to carbon ratio, because the amount of hydrogen permeates is less compared to the total hydrogen produced as it is possible to see in figure 5.7. The explanation could be found in the fact that the steam cannot cross the hydrogen membrane so the retentate increase more than the hydrogen permeate and the separation factor decreases with the steam to carbon ratio.

![Figure 5.7 Hydrogen recovery and separation factor with steam to carbon ratio](image)

**5.5 Results for the effect of velocity**

The final experiment has the purpose to understand what happens to hydrogen production when the velocity is changed, thus the residence time in the bed. The table 5.7 describes the results of FBR with Delphi model and with experiments.

**Table 5.7 Results of model and experiments for FBR changing the velocity**

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>3.64</td>
<td>0.35</td>
<td>2.24</td>
<td>3.96</td>
<td>789.27</td>
<td>0.4023</td>
<td>0.4049</td>
</tr>
<tr>
<td>4.38</td>
<td>0.42</td>
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When the ratio between the superficial gas velocity and the minimum fluidization velocity is changed, also the volumetric flow is changed. In FBR experiments and model are near, so the reactor works in a good way.

For all the cases studied, the methane conversion is higher in the MFBR than in FBR and also for the effect of velocity it happens. The figure 5.8 describes all the results obtained while the table 5.8 contains all the results for membrane fluidized bed reactor.

![Figure 5.8 Comparison between FBR and MFBR with model and experiments changing the velocity condition](image)

**Figure 5.8 Comparison between FBR and MFBR with model and experiments changing the velocity condition**

The main remark concerns that if the velocity is greater, the methane conversion is reduced due to a decrease in residence time as it is possible to see in figure 5.9.

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**Table 5.8 Results of model and experiments for MFBR changing the velocity**
Figure 5.9 Residence time with the superficial gas velocity

As already said, since the velocity is increased, the methane stay less time in the reactor and it means less hydrogen is produced, it could explain why the hydrogen recovery and separation factor decrease with the velocity, as it is shown in figure 5.10.

Figure 5.10 Separation factor and hydrogen recovery factor with the velocity
Chapter 6
Conclusion and future studies

Solid circulation rate is a key parameter in chemical looping systems since it is the responsible of the transport of heat flux help the methane conversion from the air reactor to the fuel reactor. Therefore, it is important to find a cheap and accurate method able to determine it experimentally. In this work three different methods have been studied and compared: standard method based on particle collection, optical methods and pressure drop methods.

The optical technique is based on the PIV-DIA method that can measure the solids holdup and particle velocity in order to obtain the solid circulation rate according to equation (1).

\[
SCR = u_p \ast \varepsilon_s \ast A \ast \rho_s
\]  

The optical method is based on a background correction that is an innovative method that has the purpose to correct inhomogeneous illuminations. The background correction for the riser and the fuel reactors is different, the first is dynamic, the second used the fixed bed system. The main disadvantage of PIV-DIA consists on the fact that is a method that can be used only for 2D reactors, because the particle velocity can be detected only for a planar area. The optical method has been successfully developed by first adjusting and then applying to all the experiments a linear relationship between the images and 3D solids hold-ups. This method works for the three columns in the 2D ICFB system and demonstrates good symmetry in the solids circulation patterns. Moreover, the measured solids hold-up are in a good agreement with the literature and also with the pressure drop method used in this work.

The pressure method is a innovative and interesting system because only knowing the pressure drop of the reactor is able to predict the solid circulation rate in the system using the equation (1) and solving the system composed of Bernoulli and Richardson and Zaki equations. The main disadvantage consists on the low accuracy of results when the system is characterized of non-spherical particles. Other methods based on pressure drop normally lack of accuracy in the literature. The novel two methods have been developed and validated in this work for cold flow measurements. They do not require expensive maintenance and can be used continuously in circulating systems without any influence on the hydrodynamics of the system.

Three different experimental methods for the measurement of solids circulation rates in a pseudo 2D internally circulating column have been studied, developed and compared in this work. SCR measured with the three methods lead to similar results within 20 % of maximum deviation and most of them within 10 %.

In order to analyze chemical looping systems in detail and connect all the information from solid circulation rate to the fuel reactor, the behavior of fluidized bed membrane reactor has been assessed via phenomenological models and comparison to experiments. The model used is Delphi7 and it was possible to find good correspondence from experimental results and modelling prediction. The main analysis consist on the trend between methane conversion and temperature that is positive, since the system is endothermic, with pressure that is negative due to the Le Chatelier principle, with composition that is positive because the system is supported with increase of reactants and with velocity that is negative since the resident time decreases leaving less time for the conversion of methane.
Possible future studies are related to the possibility of finding a new pressure method that can predict the solid circulation rate for non-spherical particles, solving the problems related to pressure fluctuations. Another important recommendation consists of extending the pressure method to 3D reactor especially to analyze how the friction losses can influence a three-dimensional system. However, this work has been carried out at room temperature and it should be also validated at high temperatures. A second important study that should be carried out consists of the possibilities to extend the analysis related to methane conversion and hydrogen production observing the influence of temperature, pressure, velocity, and composition on the membrane-assisted chemical looping reforming. This system is quite innovative because of the possibility to produce pure hydrogen, in an autothermal way and with CO2 capture. It should be interesting to couple the information of SCR into the model to simulate the MA-CLR with two reactors and also to verify the findings at high temperature and under reactive conditions.
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<td>a</td>
<td>Width of the column</td>
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<td>A_c</td>
<td>Section of the riser column</td>
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<tr>
<td>b</td>
<td>Depth of the column</td>
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<td>C_D</td>
<td>Drag coefficient</td>
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<td>D</td>
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<tr>
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<td>Particle diameter</td>
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<tr>
<td>d_p*</td>
<td>Dimensionless Particle diameter</td>
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<td>Darcy frictional factor</td>
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<td>g</td>
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Abbreviations

SCR          Solid circulation rate
MA-CLR   Membrane assisted chemical looping reforming
SMR          Steam methane reforming
TPES   Total primary energy supply
FBMR       Fluidized bed membrane reactor
ASU         Air separation unit
FR          Fuel reactor
CCS         Carbon capture and storage
WGS         Water gas shift
PSA        Pressure swing adsorption
CLC        Chemical looping combustion

References:


