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# Gas Switching Reforming for syngas production with iron-based oxygen carrier-the performance under pressurized conditions

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ABSTRACT

A four-stage Gas Switching Reforming for syngas production with integrated $CO_2$ capture using an iron-based oxygen carrier was investigated in this study. The oxygen carrier was first reduced using dry methane, where high methane conversion rate was achieved producing $CO_2$ and steam. Following the reduction stage is a transition to syngas production in an intermediate stage that begins with partial oxidation of methane while methane cracking dominates the rest of the stage. This results in substantial carbon deposition that gasifies in a subsequent reforming stage by cofeeding steam and methane, contributing to more syngas yield. Some of the deposited carbon that could not gasify during the reforming stage slip to the oxidation stage and get combusted by oxygen in the air feed to release $CO_2$, thereby reducing the $CO_2$ capture efficiency of the process. It is in this oxidation stage that heat is being generated for the whole cycle given the high exothermicity nature of this reaction. Methane conversion was found to drop substantially in the reforming stage as the pressure increases driven by the negative effect of pressure on both carbon gasification by steam and on the steam methane reforming. The intermediate stage (after reduction) was found less sensitive to the pressure in terms of methane conversion, but the mechanism of carbon deposition tends to change from methane cracking in the POX stage to Boudouard reaction in the reforming stage. However, methane cracking shows tendency to reduce substantially at higher pressures. This is a very interesting result reflecting that high-pressure operation would remove the need for a reforming stage with cofeeding of steam as no carbon would have been deposited in the POX stage.



## Introduction

Fossil energy consumption has steadily increased in recent decades, due to continuous increase in global energy demand, leading to rise in $CO_2$ emission [1]. With the rising concerns of global warming and associated climate change [2], development of affordable, clean and reliable energy sources is of high priority. Natural gas conversion into cleaner energy carrier, such as hydrogen, is seen as one of the most sustainable

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**Nomenclature**

*Abbreviations*

| | |
|---|---|
| BET | Brunauer–Emmett–Teller |
| BSE | Backscattered Electron |
| CCS | Carbon Capture and Storage |
| CFB | Circulating Fluidized Bed |
| CLC | Chemical Looping Combustion |
| CLR | Chemical Looping Reforming |
| EDS | Energy-Dispersive Spectroscopy |
| GSC | Gas Switching Combustion |
| GSR | Gas Switching Reforming |
| GST | Gas Switching Technology |
| OC | Oxygen Carrier |
| OXI | Oxidation |
| POX | Partial Oxidation |
| PSA | Pressure Swing Adsorption |
| RED | Reduction |
| REF | Reforming |
| SEM | Scanning Electron Microscope |
| SMR | Steam Methane Reforming |
| XRD | X-Ray Diffraction |

*Symbols*

| | |
|---|---|
| $C_{deposition}$ | Carbon deposition |
| $Carbon\_dev$ | Carbon deviation |
| $n_{C\_deposited}$ | Mole of C deposited |
| $n_{C,in}$ | Total mole of C fed |
| $n_{C,out}$ | Mole of C at the gas outlet. |
| $n_{CO,out}$ | Mole of CO at the gas outlet. |
| $n_{CO_2,out}$ | Mole of $CO_2$ at the gas outlet. |
| $n_{fuel,out}$ | Mole of fuel at the gas outlet. |
| $n_{fuel,in}$ | Mole of fuel fed |
| $n_{fuel,converted}$ | Mole of fuel converted |
| $n_{H_2,out}$ | Mole of $H_2$ at the gas outlet. |
| $\gamma_{fuel}$ | Fuel conversion |

options, given its projected 45% increase in global production and demand by 2040 [1]. Steam methane reforming (SMR) process is widely used for industrial conversion of natural gas to syngas ($CO + H_2$), but it is associated with high $CO_2$ emissions, due to its highly endothermic reaction (R1 and R5) requiring heat supply by fossil fuel combustion. Chemical looping reforming (CLR) has been demonstrated as a promising technology integrating the combustion (for heat supply) and reforming steps into a single process, thereby facilitating $CO_2$ capture at minimal energy penalty [3–5]. This technology was first applied to combustion for capturing $CO_2$ [6,7] where the typical configuration consists of two interconnected fluidized bed reactors with a metal oxide (oxygen carrier) circulating between them to transport oxygen from air to the fuel reactor for oxy-combustion. In this way, a pure $CO_2$ stream is produced (free of $N_2$) ready for compression and storage [8,9] (Fig. 1). The low energy penalty of chemical looping relative to other CCS technologies has led to the extension of the principle to other energy intensive processes such.

Traditionally, research on CLR has focused on developing suitable oxygen carriers. It is not surprising that Ni-based oxygen carriers were identified as the best performing, owing to the high catalytic activity of metallic nickel for methane reforming [16–18]. The suitability of other environmentally friendly oxygen carriers, such as Fe–, Mn– and Cu-based was also investigated [19–28]. Fe-based oxygen carriers have shown acceptable performance, with good selectivity to syngas when reducing $Fe_3O_4$ to FeO [19]. Further improvement in reactivity and selectivity to syngas was achieved by doping the Fe-based oxygen carrier (OC) with promotors such as NiO [19]. Fe-based solids oxides such as Ce–Fe and La–Fe have also been reported to exhibit high selectivity of methane conversion to syngas, resulting from the intensification of oxygen mobility occurring in the Fe-based solid oxides [29–31].

As for the contacting system, given the necessity of high pressure operation for maximizing energy efficiency and competitiveness with other $CO_2$ capture technologies [32], the circulating fluidized bed (CFB) configuration is unlikely to be suitable. Stable solids circulation between the two interconnected reactors would be difficult to achieve under pressurized conditions given that each reactor should be pressurized independently, while it is essential to fulfill the heat and mass balance of the chemical looping process. Any instantaneous pressure imbalance between the reactors may induce instabilities in solids circulation and result large leakages through the sealing devices, thereby increasing explosion risks. To date only one pilot scale experimental study on pressurized chemical looping combustion (CLC) in an interconnected fluidized bed configuration has been completed [33], despite the predicted benefits of such technology in terms of increased energy efficiency [34]. Apart from these operational challenges, there is additional cost and complexity associated with separation systems like cyclone and loop seals.

Attempts have followed in recent years to address these issues where several reactor configurations with no external solid circulation have been proposed and tested [35–39]. Among these, the "Gas Switching Technology (GST)" has a high potential in minimizing the scale up challenges of pressurized chemical looping. This technology employs a single dense fluidized bed reactor operating under bubbling/turbulent regimes, and avoids the circulation of solid oxygen carrier by alternating the feeds of the oxidizing and reducing gases to complete the different reactions involved in the chemical looping process, while ensuring inherent $CO_2$ capture (Fig. 1b). The GST technology has been proposed for heat [40,41] and hydrogen production with integrated $CO_2$ capture [8,9]. Experimental studies have proved ease of operation of this technology under atmospheric and pressurized conditions [8,9,42].

### *Gas Switching Reforming*

The GST technology was extended to methane reforming for syngas production with integrated $CO_2$ capture, the so-called Gas Switching Reforming (GSR) process, as an alternative to the CLR process that uses the interconnected fluidized bed reactors [8,9]. Similar to CLR (Fig. 2a), the typical GSR cycle consists of an air stage where heat for the endothermic reforming reaction is generated through the exothermic

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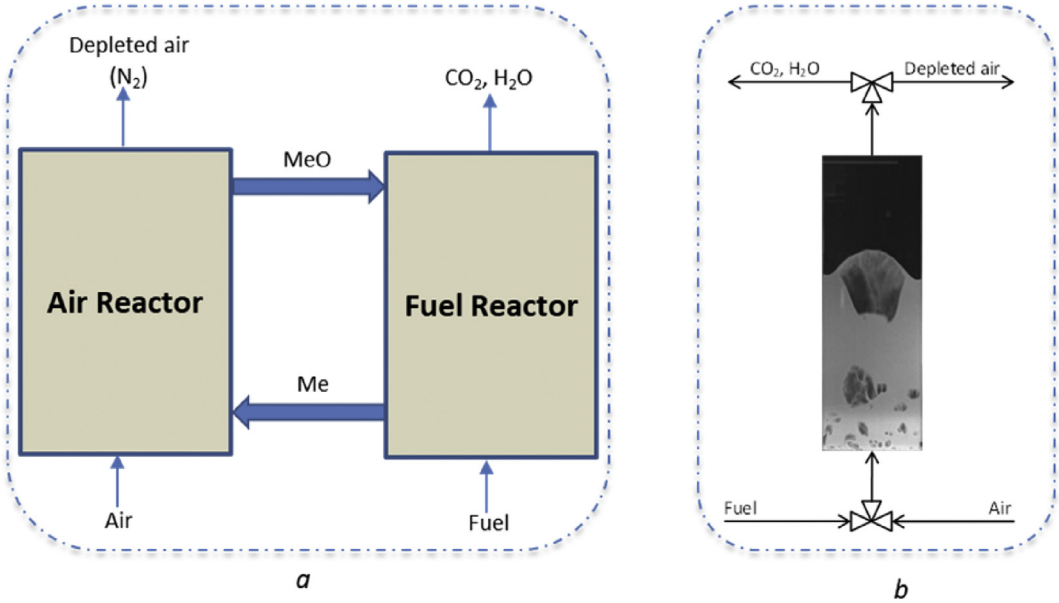


**Fig. 1 – Chemical looping combustion. (a: Conventional CLC scheme. b: Simplified GSC scheme). as reforming, through the so-called CLR [3,4]. This process has successfully been demonstrated at lab and pilot scales under atmospheric conditions [10–18].**

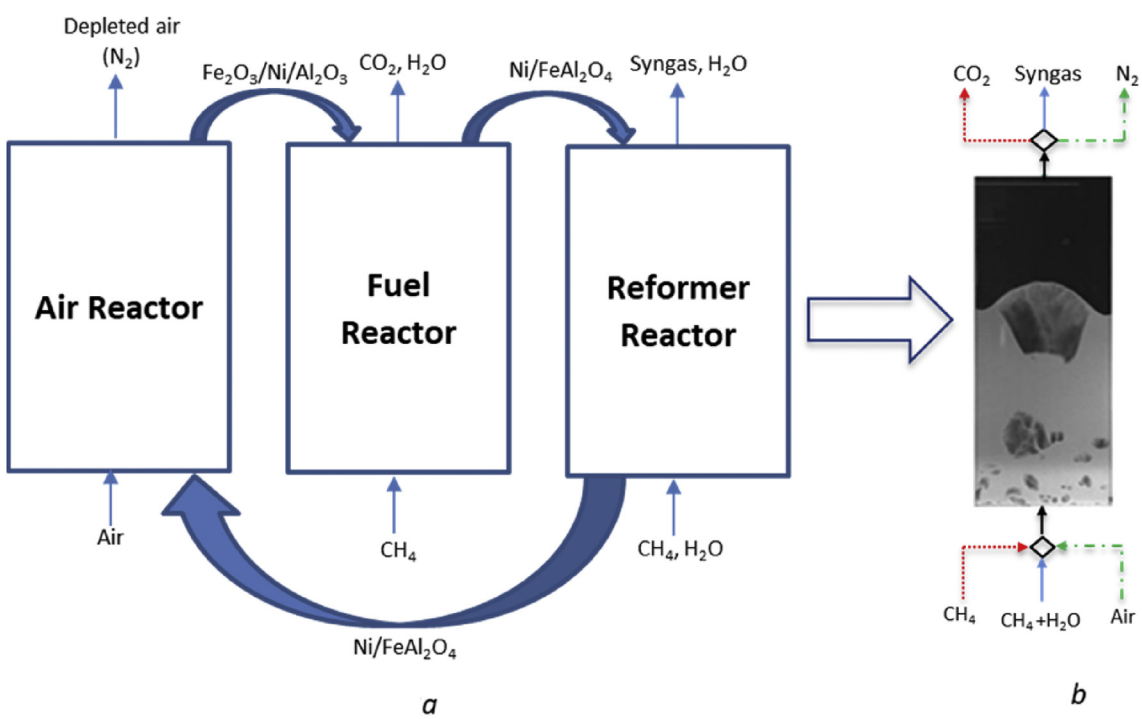


**Fig. 2 – Conceptual scheme for autothermal syngas production with integrated $CO_2$ capture using the three-stages chemical looping reforming technology. (a): Conventional CLR process arrangement and (b): the simplified Gas Switching reforming, GSR, under investigation in this paper.**

oxidation reaction. The heated oxygen carrier is then exposed to a feed of $CH_4$ in the fuel stage where a simultaneous reduction of the oxygen carrier and methane reforming to syngas take place (Fig. 2b). In this case, the oxygen carrier should also play the role of a catalyst for methane reforming. The major advantage of GSR process is the efficient use of the reaction heat produced during the oxidation stage for the endothermic reforming stage since the reactions occur in a single reactor vessel facilitating autothermal operation of the process [43]. GSR was first demonstrated using a Ni-based oxygen carrier that has shown a very good performance both in the oxidation and reduction stages [8]. This oxygen carrier exhibited an interesting behaviour in the fuel stage showing two distinct sub-stages, where pure combustion of

methane takes place in the first one (oxygen carrier reduction), while pure selectivity to syngas takes place in the second. This behaviour opens the possibility for feeding PSA-off gases to the reduction sub-stage, thereby maximizing fuel.

Conversion in the GSR process [26] . Another benefit of the use of PSA-off gases in the reduction sub-stage of GSR is the exothermicity of $H_2$ and CO reactions with the oxygen carrier, that reduces the temperature variation in the GSR cycle, thereby resulting in improved fuel conversion [8]. The three-stage GSR configuration, using CO in the reduction stage, $CH_4$ in the reforming and air in the oxidation stage was also demonstrated experimentally [8]. GSR process through a four-stages configuration has also been proposed (Fig. 3) with the major reactions at different stages shown in Fig. 4. Like other gas switching concepts, GSR faces a challenge from undesired mixing when switching the inlet feed gases, which causes some $N_2$ to leak into the fuel stage and some $CO_2$ to escape to the atmosphere with the depleted air. This leakage is small for reforming concepts though; for example, reactor modelling in a previous study on GSR showed that 97% $CO_2$ capture could be achieved despite this undesired mixing [26] .

The behaviour of GSR using three Fe-based oxygen carriers, supported on commercial alumina ($Fe-Al_2O_3$, $Fe-Ce-Al_2O_3$ and $Fe-Ni-Al_2O_3$), has recently been investigated [44] . The three of them have shown very distinct reduction and reforming stages, similar to the pure Ni-based oxygen carrier tested previously [8], with high conversion of methane to $CO_2$ in the reduction. As expected, the $Fe-Ni-Al_2O_3$ outperformed in the reforming showing methane conversion to syngas close to equilibrium at 800–850 °C. The oxidation and reduction mechanisms of the oxygen carrier with $Fe-Al_2O_3$ have been found to follow **R.1** and **R.2** (see Fig. 4) as revealed by XRD analysis [44] . The phases present after reduction are solid solutions of spinel structured oxides of the general form $M_3O_4$, where M = Fe, Ni, or Al, where in all these phases, iron was present as $Fe^{2+}$ or as a mixture of $Fe^{2+}$ and $Fe^{3+}$ with no evidence of presence of FeO, NiO or metallic Fe or Ni.

For the Ni-free Fe-based oxygen carrier, steam methane reforming occurs following heterogeneous gas-solid reactions. The highly reduced oxygen carrier particles are oxidized by steam and $CO_2$ to form $H_2$ and CO (**R.5** to **R.9**) as shown in Fig. 4; the oxidized sites immediately reduces with the incoming $CH_4$ to result in a steady state steam reforming that can continue indefinitely as long as heat is supplied to drive the overall endothermic reaction system [44] . As for $Fe-Ni-Al_2O_3$ it is likely that steam methane reforming mainly occurs following reactions **R.6** and **R.7** (Fig. 4), due to the presence of nickel [44] after the oxygen carrier is sufficiently reduced to $NiFeAl_2O_4$ (the XRD data of the reduced $Fe-Ni-Al_2O_3$ is shown in Fig. 5.

This study further investigates the GSR with the NiO promoted oxygen carrier, $Fe-Ni-Al_2O_3$, developed and tested in Zaabout et al., 2018 [44], where the focus falls on the effect of the operation pressure. The prospects of exploiting methane cracking mechanism **R.4** (Fig. 4), in hydrogen production with integrated $CO_2$ capture through GSR is also explored in this study through a four-stages GSR process (Fig. 3). In addition to the introduction and conclusion sections, this paper has two other main sections: i) experimental set-up ii) results and discussion.

## Experiment and methods

### *Experimental setup*

A fluidized bed reactor used for the GSR experiment consists of a cylindrical column (5 cm in inner diameter and 50 cm in

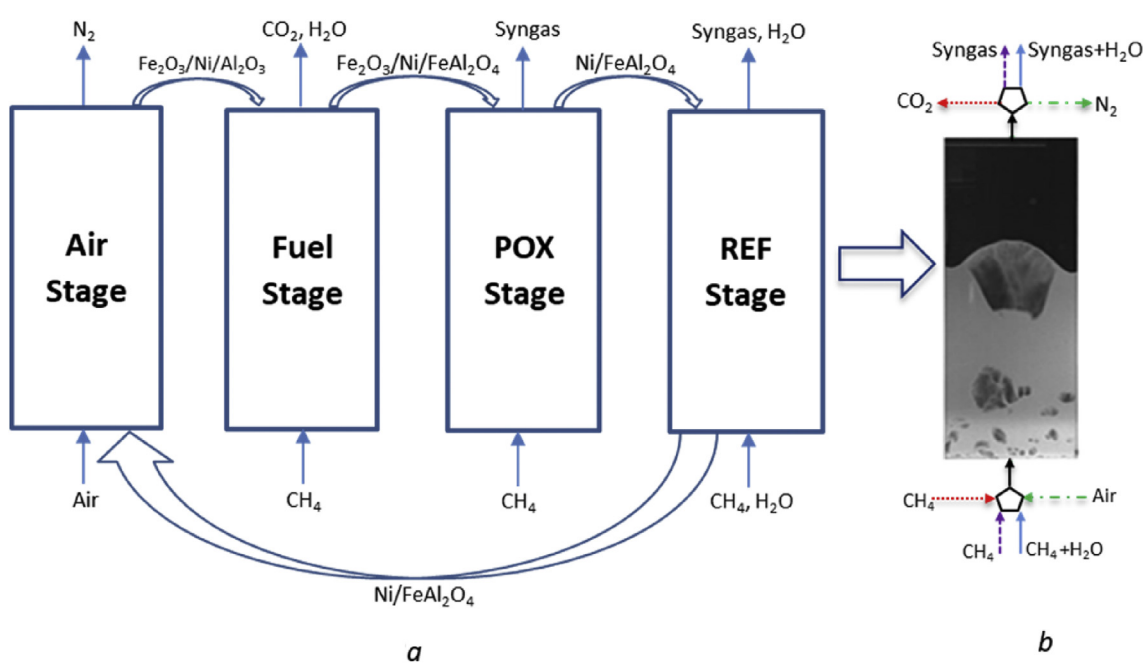


**Fig. 3 – Proposed 4-stage configuration of autothermal syngas production with integrated $CO_2$ capture using a four-stages chemical looping reforming technology. (a) Conventional CLR process arrangement and (b) The simplified Gas Switching Reforming, GSR, under investigation.**

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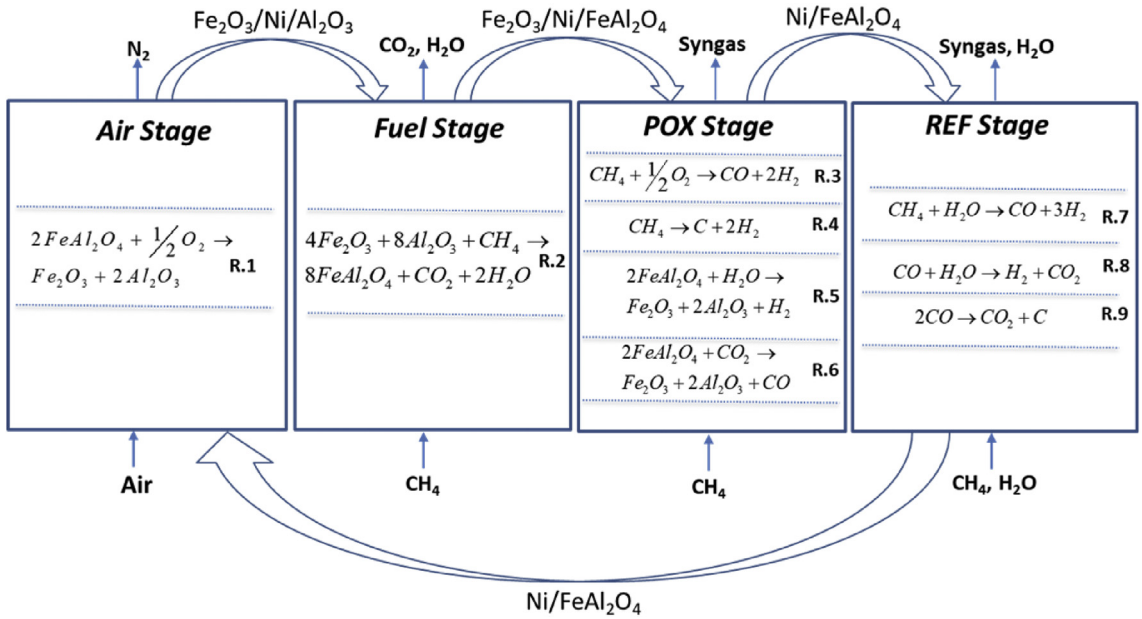


**Fig. 4 – The major reactions at different stages of a four-stage chemical looping reforming technology under investigation.**

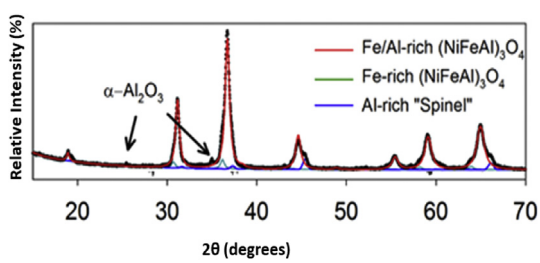


**Fig. 5 – Fitted XRD data of the sample (Fe–Ni–$Al_2O_3$) after 30 min final stage reduction at 800 °C [46].**

height) and a freeboard zone as shown in Fig. 6. A fluidized bed is desired to achieve good mixing and temperature distribution [45–47] . The freeboard zone consists of an expanding conic zone (from 5 cm in the lower end diameter to 10 cm at the top end) followed by a cylindrical part to minimize particles entrainment. The total height of the reactor, including the body and the freeboard, is 90 cm. The reactor vessel was made of Inconel 600 to withstand high temperature gas-solids reactive flows (up to 1000 °C). A porous plate with 20 μm mean pore size and 3 mm thickness, made from Inconel 600, was used as a gas distributor. Heating was done externally through electrically heating elements wound round the reactor vessel to heat up the reactor to a target temperature before starting autothermal GSR process. 25 cm thick insulation was applied to the reactor, combining blankets and vermiculate. The reactor was designed to operate at elevated pressures (up to 10 bar) and was pressurized using a back-pressure valve. Mass flow controllers from Bronkhorst BV were used for feeding gases to the reactor. A three-way electrical valve was used to separate the air and fuel feeds, and to switch between them for cycling reducing and oxidizing conditions in the reactor. A cooler was installed at the outlet of the reactor to cool down the stream of hot gases before sending it to the vent. The gas composition was measured using ETG syngas analyzer connected to.

The outlet gas stream. The analyzer can sample gases only under atmospheric pressure, which means that in our case the gas had to be sampled after the back-pressure valve. It is necessary to mention that the setup does not allow direct measure steam due to condensation in the heat exchanger. However, the quantity of steam could be quantified through $H_2$ balance. The temperature was measured at two positions in the reactor, 2 cm and 20 cm above the gas distributor using two thermocouples inserted through the middle axis of the reactor. All the measurement instruments and flow controlling devices were controlled through a LabVIEW application. The LabVIEW application was also used for data acquisition and storage.

### *Oxygen carrier*

Spherical gamma-alumina particles from Sasol (Puralox SCCa 150/200) were applied for wet impregnation of concentrated aqueous ammonium iron(I) citrate solution (~50 g/100 g water) aiming to form nanostructured iron oxide inside the mesoporous alumina structure after heat treatment. The iron precursor was partly substituted by nickel(II) nitrate hexahydrate to form iron oxide-nickel oxide composite structure. Homogenous distribution of the active metal oxides throughout the porous particles was obtained by wet impregnation with subsequent drying steps at 120 °C after each step up to a theoretical loading of ~10 wt% metal oxide, followed by heat treatment for 5 h at 500 °C (60 °C/h) in ambient air. This procedure was repeated until a theoretical loading of the active elements (Fe and Ni) was 1:1 by weight compared to Al in the porous alumina structure. The theoretical Fe:Ni ratio were 2:1 by weight. After the final impregnation and heat treatment steps, the as produced particles were sieved (100 μm) to remove fines prior to further analysis and testing. The particle size distribution range was 100–450 μm.

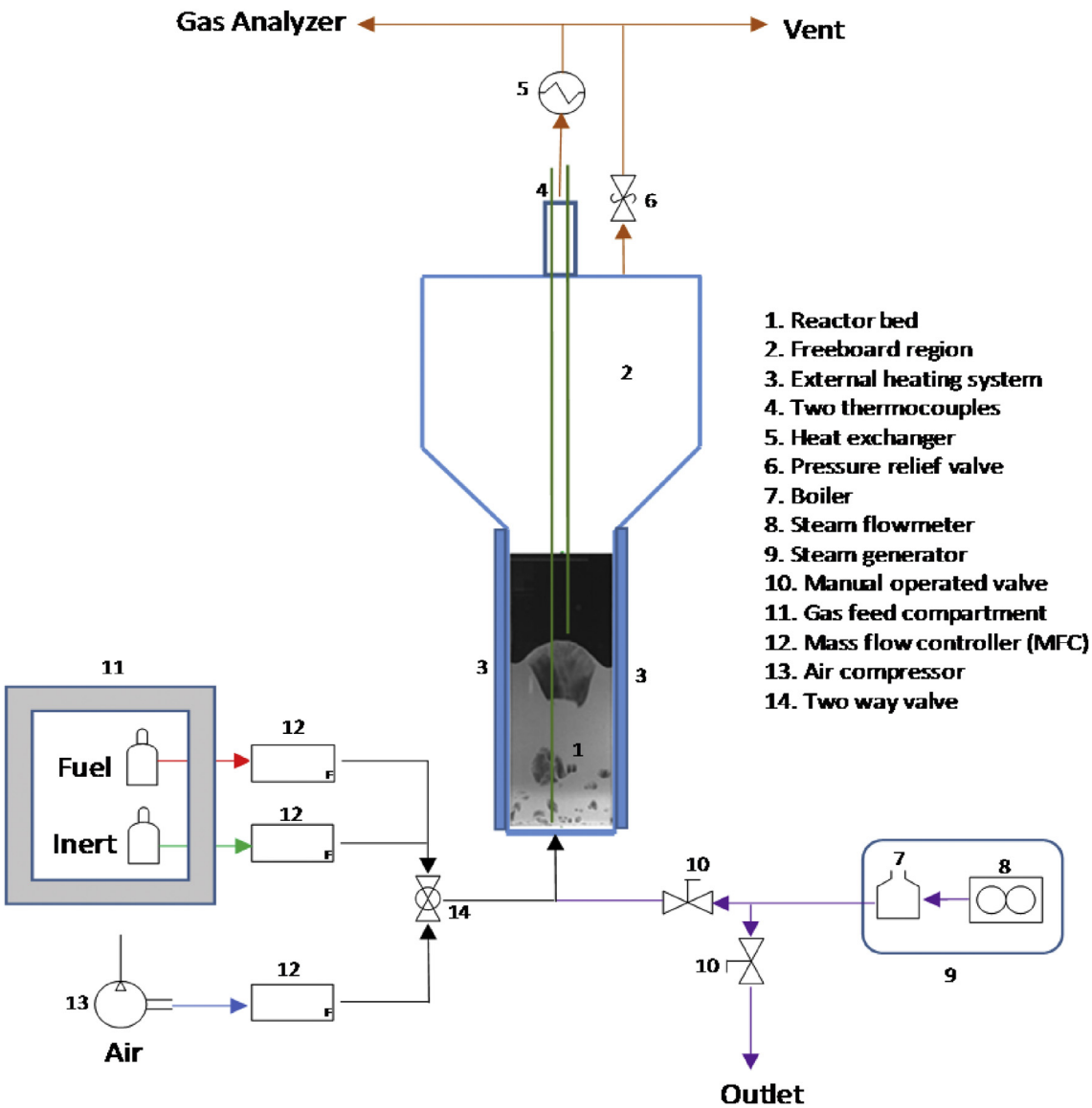


**Fig. 6 – GSR Experimental setup.**

SEM/EDS analysis on particles after sieving indicated a homogenous distribution of the Fe and Ni throughout the porous alumina structure, as seen in Fig. 7 respectively. The measured loading of active elements (Fe + Ni): Al ≈ 0.8:1 by weight which is slightly lower than the aimed value of 1:1. This reflects the loss of active material by sieving, in form of fines which are loosely deposited on the surface of the particles. The Fe:Ni ratio was found to be ~2:1, as anticipated. The BET surface areas of the produced Fe–$Al_2O_3$ and Fe–Ni–$Al_2O_3$ impregnated particles were measured to 102.9 and 97.2 $m^2/g$, respectively. In comparison, the bare alumina support particles had a BET surface area of 206.0 $m^2/g$.

### *Methodology*

The GSR concept operates in a cyclic mode by alternating air and fuel feeds to the reactor. During experiment, various gas was fed to carry out reduction, reforming and oxidation reactions in a bubbling fluidized bed of solid oxygen carrier to produce syngas and pure $CO_2$ ready for storage or further utilization at the fuel stage. A fluidized bed was used to ensure good heat transfer and manage thermodynamic equilibria constraints [48] . About 300 ml of the oxygen carrier was placed initially in the reactor.

The GSR experiments were performed at different operating pressures ranging from 1 to 5 bar at 800 °C. Three-stage process (reduction, reforming and oxidation stage) was designed as explained in section Gas Switching Reforming to complete a redox cycle. The cycle starts with the reduction stage where 0.8–4 nl/min of $CH_4$ was fed into the reactor between 12 and 2.4min to reduce the $Fe_2O_3$/Ni/$Al_2O_3$ oxygen carrier for the catalysis of the steam methane reforming and other competing reactions as shown in **R.5** to **R.9** (Fig. 4). After the reduction stage, the reforming stage starts through a combination of catalytic reforming and other heterogeneous reduction reactions to produce syngas (CO and $H_2$). A feed of air follows to oxidize back the reduced oxygen carrier following an exothermic reaction that builds up heat in the

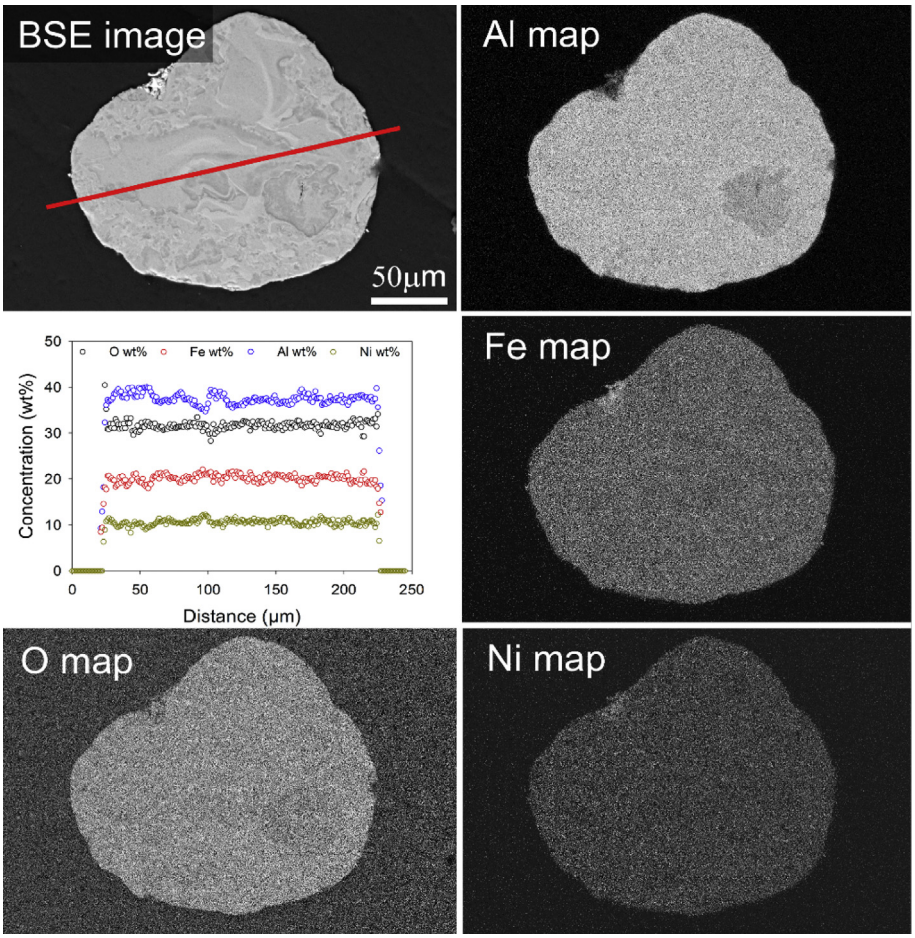


**Fig. 7 – Backscattered Electron (BSE) image of a catalyst carrier cross section with corresponding x-ray element maps and quantitative line scan data. The linescan data was collected along the red line indicated on the BSE image. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)**

reactor. The generated heat is then being used in the subsequent fuel stage with mainly endothermic reactions (reduction and reforming). Five seconds purging with an inert gas is applied between the air and fuel stages to avoid direct contact between them in the feed pipes, thereby eliminating the risk of explosion. Experiments for each operating condition were completed for at least ten redox cycles to ensure repeatability.

As mentioned earlier, real time temperature and pressure measurements were collected using a Labview application while online gas composition was measured using an ETG Syngas analyzer. The reactor performance at different temperature was evaluated using the following measures: fuel conversion, CO and $H_2$ selectivity (expressed as $H_2$/CO and $H_2$/C ratios), degree of carbon deposition, as described in next section. These performance measures are defined as specified in Eqs. (1)–(5). The experimental results were compared with equilibrium predictions.

### *Reactor performance measures*

The objective of the GSR process is to convert a hydrocarbon fuel ($CH_4$ in this study) to syngas ($H_2$ and CO). Therefore, it is desired to maximize the fuel conversion in the reduction stage, maximize $CH_4$ conversion at the in all stages. Thus, fuel conversion is an important measure to evaluate the performance of GSR process. This can be quantified as follows:

$$\gamma_{fuel} = 1 - \frac{n_{fuel,out}}{n_{fuel,in}} \tag{1}$$

CO and $H_2$ are the major constituents of syngas that determine quality and possible usage of syngas. It is therefore important to determine the syngas ($H_2$:CO) ratio as:

$$\frac{H_2}{CO} = \frac{n_{H_2,out}}{n_{CO,out}} \tag{2}$$

Significant carbon deposition could block the active sites of the oxygen carrier thereby leading to drop in activity. The deposited carbon would be released in the oxidation stage in form of $CO_2$. Carbon deposition is therefore and important performance measure and can be quantified as:

$$C_{deposition} = \frac{n_{C\_deposited}}{n_{fuel,converted}} = \frac{n_{C,in} - n_{C,out}}{\gamma_{fuel} * n_{fuel,in}} \tag{3}$$

Knowing the mechanism (methane cracking or Boudouard reaction) responsible for carbon deposition is important for process improvement. These mechanisms could be identified using $H_2$/C ratio. High $H_2$/C ratio (>2.5) indicates that carbon deposition is mainly through methane cracking and vice versa.

$$\frac{H_2}{C} = \frac{n_{H_2,out}}{n_{CO_2,out} + n_{CO,out}} \quad (4)$$

The deposited carbon in previous stage would gasify in presence of steam thus increasing syngas yield. This phenomenon was quantified using carbon deviation as described in Eq. (5). The parameter is deduced from carbon balance with negative values indicating gasification phenomenon while positive values indicate no gasification.

$$Carbon\_dev = \frac{n_{C,in} - n_{C,out}}{n_{C,out}} = \frac{n_{C,in}}{n_{C,out}} - 1 \quad (5)$$

## Result and discussion

### *The behaviour of the GSR concept*

A three-stages (reduction, reforming and oxidation) cycle was designed to demonstrate the GSR using Fe–Ni/$Al_2O_3$ oxygen carrier at 1 bar and 800 °C as shown in Fig. 8. The cycle starts with the reduction stage where dry $CH_4$ is fed to reduce the oxygen carrier, showing high $CH_4$ conversion (~97.61% close to equilibrium prediction) with significant yield of $CO_2$ over several repeatable cycles. As $CH_4$ conversion starts to drop at the end of the reduction stage, steam is.

co-fed with $CH_4$ to start the reforming stage, showing an immediate positive effect by increasing back $CH_4$ conversion (beyond 90%) to syngas ($H_2$ and CO) instead of $CO_2$ as was happening in the reduction stage. $CO_2$ yield in this stage indicates the presence of water-gas shift reaction. Given that the reactions in both the reduction and reforming stages are endothermic and limited by equilibrium, it is necessary that the reforming stage is followed by an exothermic oxygen carrier oxidation stage with air feed, to provide the heat required for $CH_4$ conversion in the consecutive stages. The oxygen conversion is complete almost in the entire oxidation stage. A switch to the consecutive reduction stage is applied just after $O_2$ breakthrough (indicating complete oxidation of the oxygen carrier) to ensure maximizing heat usage by the endothermic reforming and reduction reactions (any further feed of air after $O_2$ breakthroughs leads to heat removal from the system).

It could, however, be observed that $CO_2$ is generated in the air stage, indicating the presence of deposited carbon from the precedents stages that combusts with $O_2$ in this stage producing $CO_2$ The estimated total carbon deposition that leaks to the atmosphere in the air stage is ~1.1% of the total converted methane in the entire fuel stage (both reduction and reforming stages). Note that no carbon deposition has been detected when steam was co-fed with $CH_4$ in the reduction stage as well [44]. Carbon deposition through methane cracking was identified as one of the main mechanisms involved in both $Fe_2O_3$ and $Fe_3O_4$ reduction with methane, leading to high hydrogen yield [49]. To explore the prospects of exploiting the methane cracking mechanism in producing hydrogen, the feed of dry methane in the reduction stages has been prolonged, before cofeeding steam. Interestingly, an additional distinct stage appears between the reduction and reforming stages (Fig. 9) where methane conversion improves back after it slows down in the end of the reduction stage, but towards syngas in this intermediate stage, rather than $CO_2$. In this stage, the $H_2$/C ratio starts at values close to 2, indicating that syngas production begins through partial oxidation of methane **R.3** (Fig. 4), but it rapidly increases to reach seven at the end of the stage, indicating that the syngas production mechanism quickly shifts to methane cracking. This is also confirmed by the transient carbon deposition showing a sharp increase in this intermediate stage. Note that methane conversion gradually decreases when methane cracking starts taking over but it remains much higher than the level obtained in the end of the reduction stage.

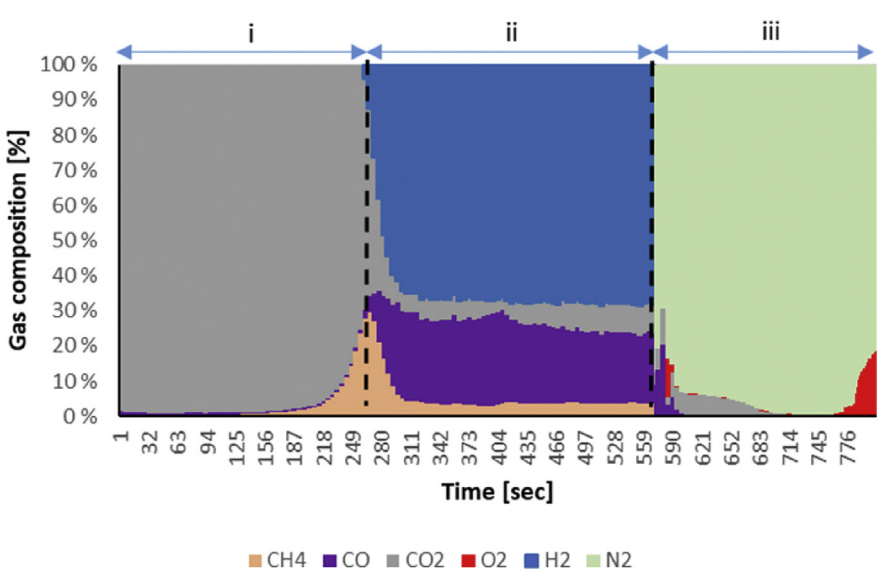


**Fig. 8 – The transient dry gas composition at the reactor outlet and $H_2$/C ratio for a GSR cycle without partial oxidation stage at atmospheric pressure and 800 °C. The GSR stages (reduction, reforming and oxidation) are numbered i, ii and iii respectively.**

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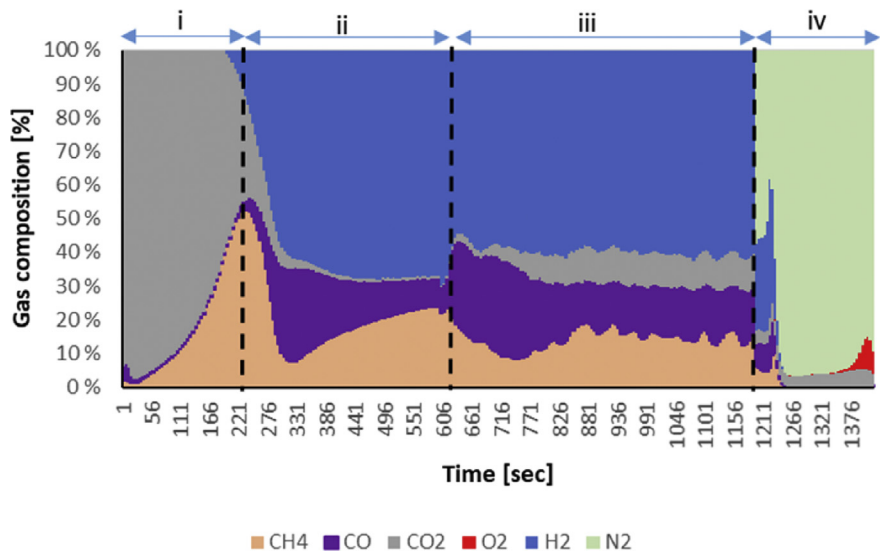


**Fig. 9 – The transient dry gas composition at the reactor outlet of a GSR cycles with partial oxidation stage at atmospheric pressure and 800 °C. The GSR stages (reduction, partial oxidation, reforming and oxidation) are numbered i, ii, iii and iv respectively.**

Mass balance calculation was completed for the reaction of $CH_4$ with $Fe_2O_3$/NiO to $CH_4$ and $H_2O$ (assuming an ideal scenario where NiO reduces to Ni while $Fe_2O_3$ reduces to $FeAl_2O_4$ as shown by XRD analysis depicted in Fig. 5). For a mass of 296 g of the Fe–Ni–$Al_2O_3$ oxygen carrier, with an active content of 35 wt% (11.5 wt. NiO and 23.5 w. $Fe_2O_3$), the total moles of $Fe_2O_3$ available for reaction is ~0.44 mol and for NiO is ~0.46 mol. For a $CH_4$ feed rate of 0.8 Nl/min ~410 s is needed to fully convert $Fe_2O_3$ to FeO (when full methane conversion is assumed). It can however be seen in Fig. 9 that the reduction stage with full selectivity to $CO_2$ is finished after only 205 s of reduction time, then syngas starts been produced. With the achieved 90% methane conversion rate in the reduction stage, only ~45% of available active content was consumed in the reduction stage, while the rest remains available for the subsequent partial oxidation (POX) and reforming stages. So, in principle enough oxygen remains available for fully converting the fed methane in the POX stage through the partial oxidation of methane, but the results show that methane cracking overtakes instead. It is likely that, the 50% reduced sites on the oxygen carrier were enough to ignite methane cracking.

An immediate sharp drop in the $H_2$/C ratio occurs (reaching values close to 2) when steam is cofed with $CH_4$ after the intermediate stage, combined with a large improvement in methane conversion (Fig. 10). Interestingly, the transient

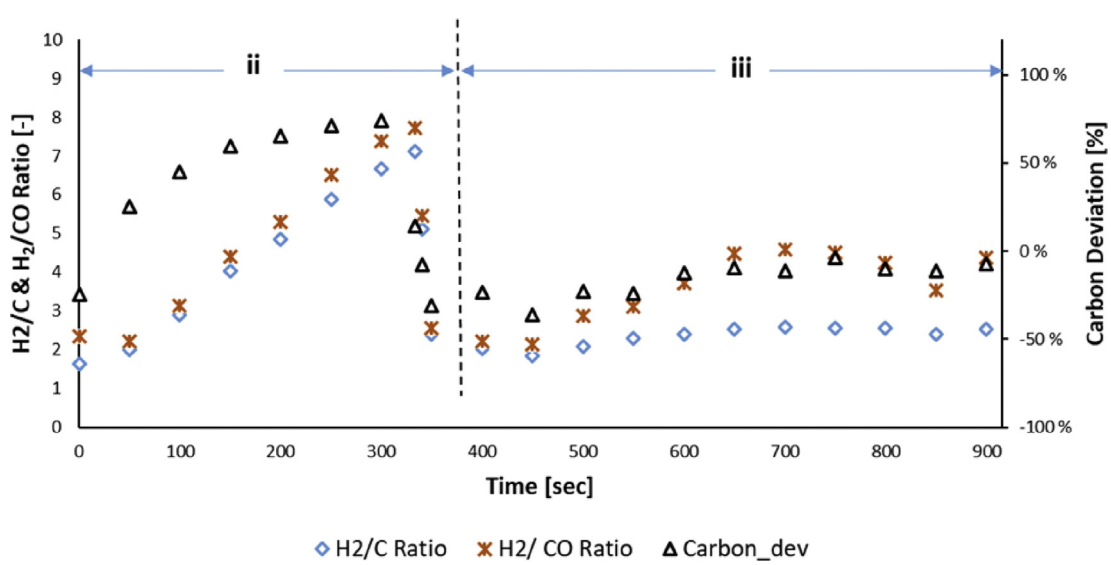


**Fig. 10 – The transient $H_2$/C ratio, $H_2$/CO syngas ratio and Carbon deviation during the POX and Reforming stage of a GSR cycles at atmospheric pressure and 800 °C. The GSR stages (partial oxidation and reforming) are numbered ii and iii respectively.**

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carbon imbalance (Eq. (5)) is negative in this reforming stage, indicating existence of a second source of syngas production, which is gasification of carbon that has deposited in the previous stage, by the steam cofed with methane. This carbon imbalance shows above 30% contribution of carbon gasification in the first third of reforming time but reduces to below 10% after, reflecting that steam methane reforming is becoming the dominating mechanism in syngas production. This is confirmed by the $H_2$/CO ratio that follows the same trend as the carbon imbalance, showing values ~2 in the first third of reforming time (high contribution of carbon gasification by steam) but increases gradually to stagnate at ~4 in the rest of the stage (methane reforming domination). $CO_2$ concentration starts very low in the reforming stage showing a gradual increase then plateaus as carbon gasification slows down, likely originating from the water-gas-shift reaction between the feed steam and the produced CO. The overall $CH_4$ conversion in this reforming stage was however lower than the case without the intermediate POX stage (Fig. 11). It could be speculated that the high amount of carbon deposition on the oxygen carrier surface increases the resistance to gas diffusion to the catalytic sites of the oxygen carrier, leading to a reduced methane conversion.

In short, large contribution of carbon gasification to syngas production occurs first when steam is cofed with methane, then steam methane reforming dominates. The integral of the carbon balance shows that almost 100% of the total carbon deposited in the POX intermediate stage gasifies with steam in the reforming stage (Fig. 12). Some of the deposited carbon is found to combust in the oxidation stage. This implies that some carbon deposition has happened already in the reduction stage with dry methane. Longer reforming stage or an additional separate stage with only steam feed could be applied to fully remove the carbon before the air stage if high $CO_2$ capture efficiency is targeted. The heat balance is however an important factor to take in consideration when designing such a cycle targeting autothermal operation.

Overall, better total methane conversion was achieved in GSR configuration with only reduction and reforming stage, with lower $H_2$/CO ratio and minimal carbon deposition (Fig. 11). However, given that the different mechanisms involved in syngas production through methane (SMR, POX, methane cracking) are affected differently by the operating pressure, the sensitivity study to the pressure was completed on the four-stages GSR cycle. This is especially important, given the well-known negative effect of pressure on steam methane reforming reaction (**R.7** as shown in Fig. 4) limited by equilibrium. As shown in Appendix 1, very high operating temperatures will be needed with the three-stages GSR process when high pressure operation is targeted. Some fundamental differences in the performance between the POX and reforming stages could already be seen at atmospheric pressure with higher methane conversion and higher $H_2$/CO during the POX stage (Fig. 13).

### *The effect of pressure*

Experiments were completed for operating pressures up to 5 bar. The feed flow rates were increased proportionally to the pressure to maintain the gas superficial velocity in the reactor constant, while the stage time was decreased similarly to maintain the oxygen carrier utilization constant. All experiments were completed at a temperature of 800 °C. In general, methane conversion has a decreasing trend with increased pressure as shown in Fig. 14. This behaviour is consistent with thermodynamics since the overall reaction during the partial oxidation stage and reforming is endothermic. Equilibrium predicts almost complete conversion for all stages up to 5 bar. However, fuel conversion was below equilibrium prediction showing that the process is limited by kinetics. Highest conversion was achieved during the reduction stage, with almost no sensitivity to the pressure, followed by the POX stage and least during the reforming stage (Fig. 14). This could be explained with the increasing endothermicity of the reaction

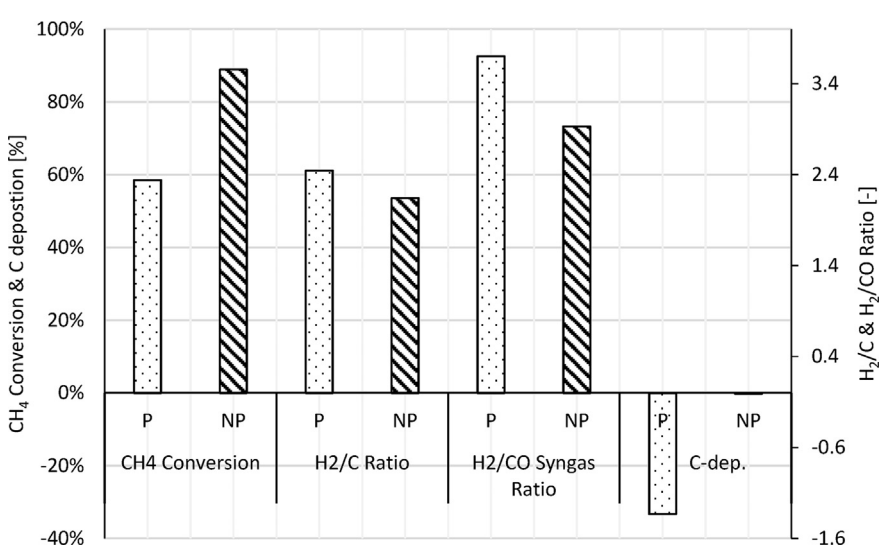


**Fig. 11 – Comparison of the performance in the reforming stage (when steam is cofed with methane) between the case with and without POX at 1 bar and 800 °C. P and NP represents the case with Partial oxidation and without partial oxidation respectively.**

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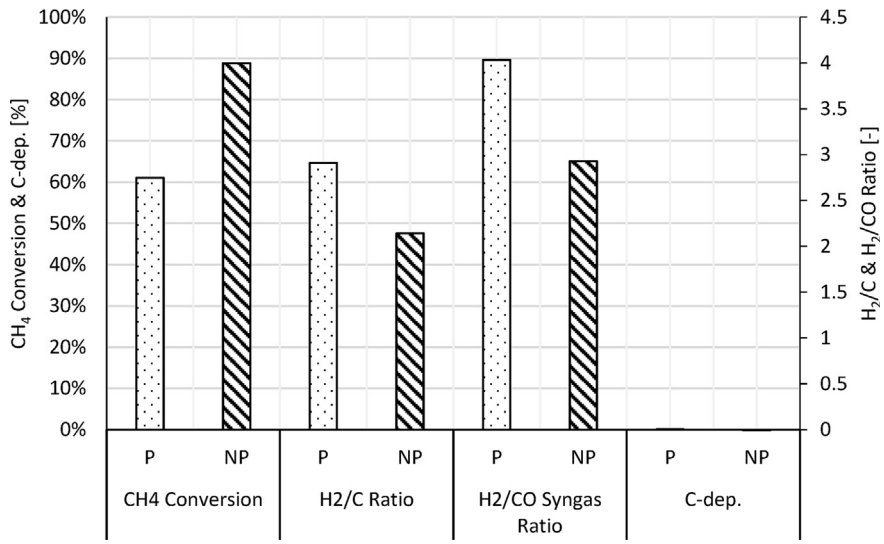


**Fig. 12 – Comparison of the performance in the syngas production stage (POX + Ref) between the case with and without POX at 1 bar and 800 °C. P and NP represents the case with Partial oxidation and without partial oxidation respectively.**

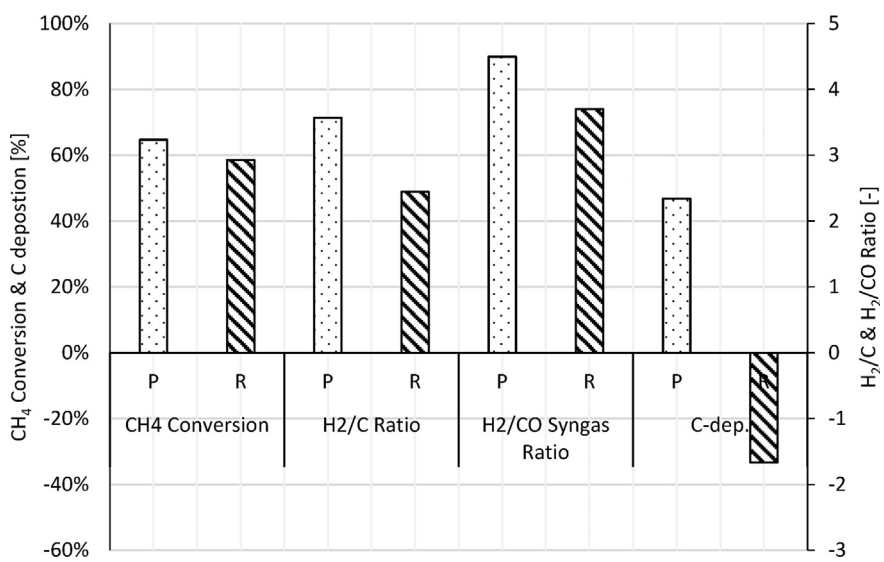


**Fig. 13 – Comparison of the performance between the POX and reforming stage for the four-stages GSR cycle (with the intermediate POX case) at 1 bar and 800 °C. P and R represent the POX and the Reforming stages respectively.**

from the reduction to the reforming stage. Pressure increase will thus result in more moles (molecules) per area within the system blocking active sites for reaction (Fig. 14). The effect of pressure is more pronounced for the reforming stage with conversion dropping by approximately 57% by increasing the pressure from 1 bar to 5 bar (Fig. 14).

The $H_2$/C and $H_2$/CO ratios reduce with pressure during the POX stage, conforming to thermodynamics as methane cracking reduces with pressure (Fig. 15). The results show however that carbon deposition does not follow the sharp trend shown on the $H_2$/C and $H_2$/CO ratios, implying a change in the dominating carbon deposition mechanism from methane cracking to Boudouard. This can be clearly seen on the $H_2/CO_2$ ratio that decreases sharply from 42 at 1 bar to 6.7 at 3 bar and further down to ~4.8 at 5 bar (Fig. 15). This means that the selectivity to $CO_2$ rapidly increases at higher pressure driven by the boudouard reaction (*R.9* as shown in Fig. 4).

As for the reforming stage, it was mentioned earlier that at 1 bar the carbon deposited in the POX stage was gasified by the co-fed steam in the subsequent reforming stage, leading to more than 30% excess of syngas production than would have originated from converted methane (Fig. 13). This is concluded from the calculated negative carbon deposition in the reforming stage, interestingly showing gasification of high percentage of deposited carbon from the previous stage (a slightly longer reforming stage would have led to total gasification of the deposited carbon). The contribution of carbon gasification to syngas production in the reforming stage reduces systematically as the pressure is increased despite the

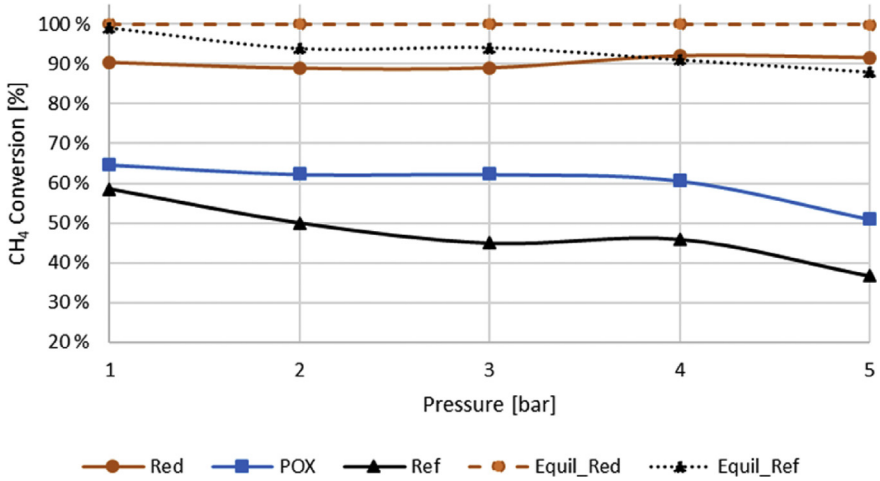


**Fig. 14 – Methane conversion at different stages as a function of pressure at 800 °C. Red represents the reduction stage, POX, partial oxidation and Ref, the reforming stage. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)**

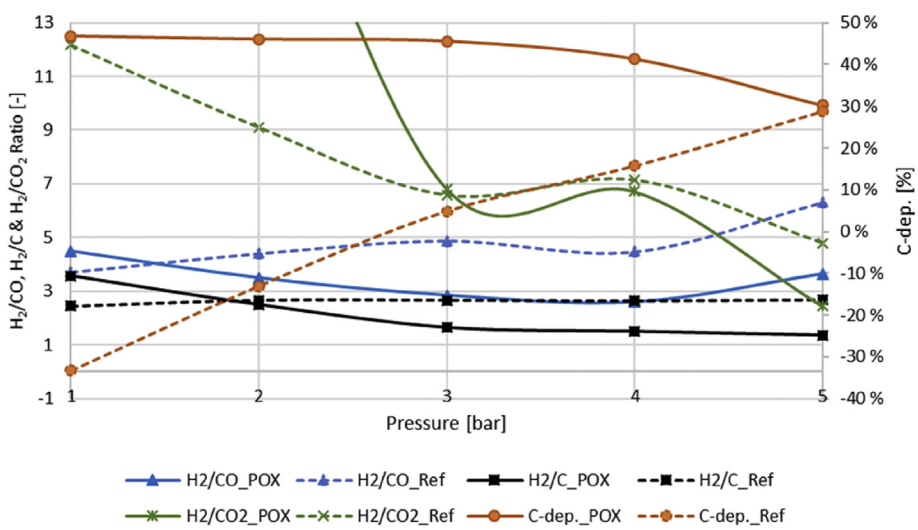


**Fig. 15 – Performance ($H_2$/C ratio, $H_2$/CO syngas ratio and carbon deposition) at different stages as a function of pressure at 800 °C. Red represents the reduction stage, POX, partial oxidation and Ref, the reforming stage. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)**

high deposition rate in the previous stage (Fig. 15). This is well in line with the thermodynamic predictions confirming the negative effect of pressure on steam gasification of carbon [50]. The carbon deposition in the reforming stage becomes positive above 3 bar reflecting the overtaking of the boudouard mechanism over steam carbon gasification as the pressure is further increased. As for the $H_2$/CO ratio, it has increased with pressure driven by the positive effect of pressure on Boudouard and Water-Gas-Shift reactions (Fig. 15). Values beyond 6 were achieved at 5 bar, which could be interesting when hydrogen production is targeted.

The low conversion of methane in this reforming stage combined with the reducing ability in steam gasification of deposited carbon, questions the usefulness of combining the POX and reforming stages for syngas production, with integrated $CO_2$ capture, when high pressure operation is targeted. Interestingly, the reducing carbon deposition in the POX, that accentuates at higher pressures, would remove the need for cofeeding steam in the subsequent stage, making the GSR process even simpler, easier to control and more energy efficient, as steam generation won't be needed. Cofeeding of $CO_2$ with methane in the POX would also help in further suppressing carbon deposition by reversing the equilibrium Boudouard reaction. In this case, contribution of methane dry reforming to syngas production should be expected due to the presence of $CO_2$ with methane on reduced Ni. The low $H_2$/CO ratio achieved in the POX makes the process better suitable to Fischer-Tropsh applications; this would be even lower if dry

reforming is contributing to syngas production if $CO_2$ is cofed in the POX. A shift and PSA steps could be applied if $H_2$ production is targeted.

Future research should focus on investigating the GSR with only the POX stage at higher pressures to confirm the trend of decreased carbon deposition at higher pressures and study the effect of $CO_2$ cofeeding on the performance in terms of methane conversion, carbon deposition, selectivity to hydrogen and CO and $H_2$/CO ratio. It is worth mentioning, that a recent study has shown that with a nonstoichiometric $CH_4$–$CO_2$ mixture feed ($CO_2/CH_4$ ratio = 0.38) to a 1 wt% Ni-entrapped $Fe_2O_3/Al_2O_3$ oxygen carrier at 900 °C, an $H_2$/CO ratio of 2.09 and high CO selectivity of 96.76% were achieved with minimized carbon deposition [51]. This study was completed at atmospheric pressure.

## Conclusion

The performance of a four-stages GSR process for syngas production with integrated $CO_2$ capture was tested using an iron-based oxygen carrier. The cycle comprises a reduction stage with dry methane (PSA-off gas could also be used), followed by a partial oxidation of methane stage (POX), then a reforming stage where steam is cofed with methane and finally the oxidation stage for heat production for the whole cycle by the exothermic oxidation reaction. Experiments were completed at 800 °C and pressure range of 1 bar – 5 bar. The oxygen carrier consisted of a Fe–Ni/$Al_2O_3$ prepared following impregnation routes. The effective active content of the oxygen carrier was 35 wt% with third of it being NiO and the other two thirds are $Fe_3O_4$.

High methane combustion rate was achieved in the reduction stage to drop in the end of the stage but increases back transitioning to syngas production instead of $CO_2$ in the reduction stage. In the beginning of the POX stage syngas was produced through partial oxidation of methane, but it shifted gradually to methane cracking, with high $H_2$/CO ratio reaching 7 at the end of the stage. This resulted in substantial carbon deposition that gasified in the subsequent reforming stage by the cofed steam, resulting in additional syngas production than estimated by the converted methane. Some deposited carbon slipped to the oxidation stage to combust with oxygen in the air feed, thereby reducing the overall $CO_2$ capture efficiency of the process.

Increased pressure has changed the carbon deposition mechanism in the POX stage from methane cracking to Boudouard, but it had a limited impact on the overall methane conversion in this stage. In parallel, increased pressure reduced the ability of cofed steam in the reforming stage for gasifying the deposited carbon which consequently magnified the negative effect of pressure on overall methane conversion in this stage, leading to substantial drop in methane conversion. Interestingly, the noticed overall reduction of carbon deposition in the POX stage with increased pressure suggests the possibility of removing the need for any feed of steam in a subsequent reforming stage, thereby maximizing the energy efficiency of the process as no expensive steam raise will be needed. It is therefore concluded that when high pressure operation is targeted, a GSR process with only three stages (RED + POX + OXI) could be best suited for syngas production with integrated $CO_2$ capture. Future research will explore further opportunities for optimizing the three-stages GSR process at even higher pressures.

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EUROPEAN COMMISSION

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## Appendix 1. Thermodynamic analysis

The equilibrium prediction of different possible reaction paths was performed by minimizing the Gibbs energy function through material balance using non-stoichiometric approach. Fifteen possible reactions have been identified and analysed. The equilibrium predictions were compared with experimental results to identify the dominating reaction path at different GSR stages. The equilibrium calculation was implemented using HSC Chemistry by feeding stoichiometric amounts of the reactants and indicating all the possible products. By minimizing free energy, the equilibrium composition at 800 °C and pressure between 1 and 5 bar were estimated. Ideal mixture was assumed and the oxygen carrier only in solid phase with the activity coefficient of unity (pure substance in condensed phase). Fuel conversion is an important parameter that determines how much fuel required across each stage. Therefore, fuel conversion was estimated following the same assumptions proposed in the article of Svoboda, Slowinski [52].

From the 2nd law of thermodynamics, the expression of the Gibbs free energy at constant temperature and pressure is given as: [53].

$$dG|_{T,p} = \sum_{i=1}^{N_{species}} \left[\frac{\partial G}{\partial n_i}\right]_{T,p,n_{j\neq i}} \tag{1}$$

Assuming ideal gas, for minimum Gibbs free energy, $dG|_{T,p} = 0$ for some $n$. It is also required that the Hessian matrix $(\partial^2 G/\partial n_i \partial n_j)$ is definitely positive. The Gibbs free energy of the reaction is calculated as follows [54]:

$$\Delta G_r = \sum \Delta G_f(\text{final}) - \sum \Delta G_f(\text{initial}) \tag{2}$$

where $\sum \Delta G_f(\text{final})$ is the sum of the Gibbs free energies of the product and $\sum \Delta G_f(\text{initial})$ is the total Gibbs energy of the reactants. The equilibrium constant is then calculated:

$$K^0(T) = \exp\left(-\frac{\Delta G_r^T}{RT}\right) \tag{3}$$

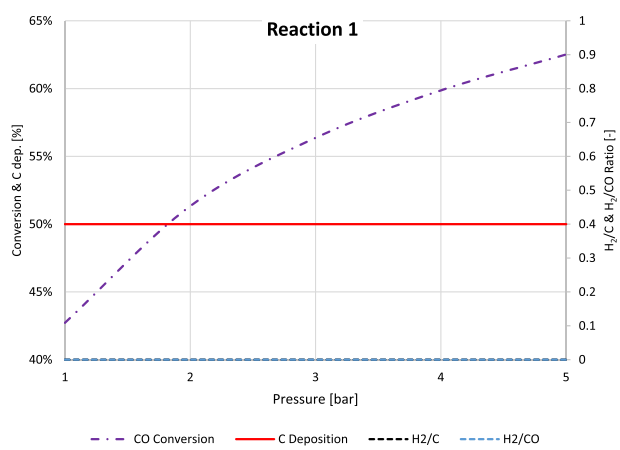
In terms of the partial pressures and activity coefficient, equilibrium constant can be expressed as:

$$K^0 = \frac{\prod(\alpha_{product\ i})^{s_i}}{\prod(\alpha_{reac\ tan\ t\ i})^{s_i}} = \frac{\prod(P_{product\ i})^{s_i}}{\prod(P_{reac\ tan\ t\ i})^{s_i}} \tag{4}$$

where $\alpha_i$ is the chemical activity of the compound $i$, $p$ is the partial pressure of the gaseous compound $i$ and $s_i$ the stoichiometric coefficient of the compound $i$.

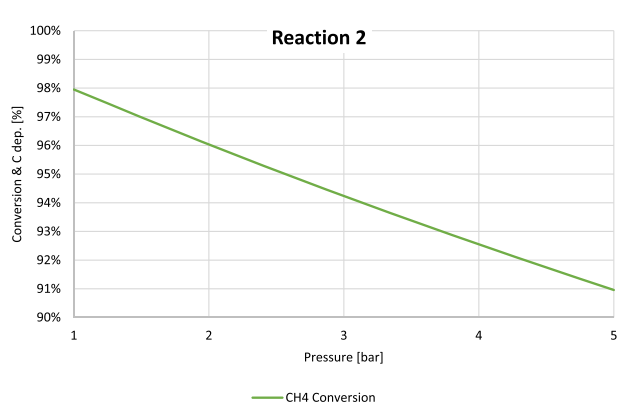
**Reaction 1**

$2CO \rightarrow CO_2 + C$



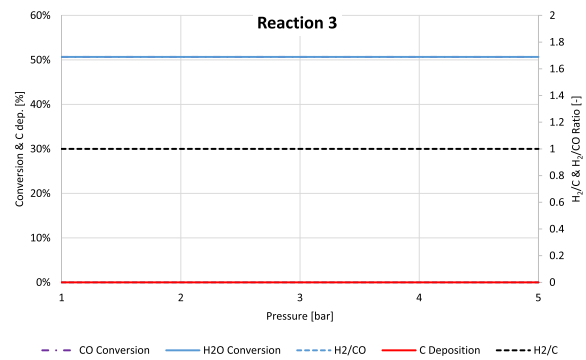

**Reaction 2:**

**Cracking.** $CH_4 \rightarrow C + 2H_2$



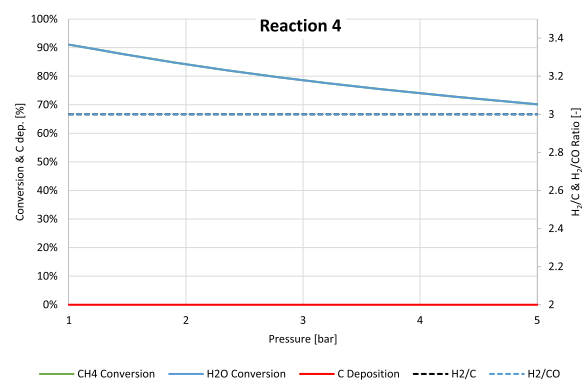

**Reaction 3:**

**Shift reaction.** $CO + H_2O \rightarrow H_2 + CO_2$




**Reaction 4:**

**SMR.** $CH_4 + H_2O \rightarrow CO + 3H_2$

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