A novel gas switching combustion reactor for power production with integrated CO₂ capture: Sensitivity to the fuel and oxygen carrier types

Citation for published version (APA):

Zaabout, A., Cloete, S., Sint Annaland, van, M., Gallucci, F., & Amini, S. (2015). A novel gas switching combustion reactor for power production with integrated CO₂ capture: Sensitivity to the fuel and oxygen carrier types. *International Journal of Greenhouse Gas Control*, 39, 185-193. <https://doi.org/10.1016/j.ijggc.2015.05.006>

Document license:
TAVERNE

DOI:
[10.1016/j.ijggc.2015.05.006](https://doi.org/10.1016/j.ijggc.2015.05.006)

Document status and date:
Published: 01/01/2015

Document Version:
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

A novel gas switching combustion reactor for power production with integrated CO₂ capture: Sensitivity to the fuel and oxygen carrier types

Abdelghafour Zaabout^a, Schalk Cloete^a, Martin van Sint Annaland^b, Fausto Gallucci^b, Shahriar Amini^{a,*}

^a Flow Technology Department, SINTEF Materials and Chemistry, Trondheim, Norway

^b Chemical Process Intensification, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology (TU/e), Eindhoven, The Netherlands

ARTICLE INFO

Article history:

Received 19 February 2015

Received in revised form 29 April 2015

Accepted 5 May 2015

Keywords:

Chemical switching

CO₂ capture

Clean power production

Dynamic fluidized beds

Thermodynamic analysis

ABSTRACT

In this paper, the gas switching combustion (GSC) concept is further investigated with a sensitivity analysis for the fuel and oxygen carrier types. The GSC concept offers an alternative to the conventional chemical looping combustion (CLC) process for power production with integrated CO₂ capture. In this concept, oxidation and reduction of the oxygen carrier take place in the same reactor by alternating air and fuel gas feeds into the reactor. This completely avoids any need for oxygen carrier circulation and thereby avoids many technical and scale-up challenges related to the looping concept. First demonstration of the concept with carbon monoxide (CO) as reducing gas and Ni-based oxygen carrier showed that the reactor could operate autothermally to continuously convert cold feed gases into hot product gases.

This work consists of two parts: Firstly, the GSC concept is further experimentally tested with syngas and methane as reducing gases on the same Ni-based oxygen carrier as used in the first demonstration. This experimental study is then followed by a more detailed thermodynamic analysis where the bed temperature variation sensitivity to the oxygen carrier and fuel is investigated.

As for the experimental study, syngas showed complete conversion with no carbon deposition, leading thereby to high CO₂ purity (95%) and capture efficiency (95%). Lower CO₂ purity was achieved (~80%) when methane was used which was mainly caused by unconverted fuel and the existence of unconverted carbon monoxide as side product. Increasing the operating temperature slightly enhanced methane conversion to 84% which is still below expectations. High CO₂ capture efficiency (95%) has however been achieved due to the absence of carbon deposition.

Thermodynamically, the influence of four different oxygen carrier materials on the temperature variation across the GSC cycle has been determined. Minimization of the temperature variation across the cycle is important in order to maximize the electric efficiency of the process and prevent turbine wear. The temperature variation across the four oxygen carriers and two fuel types investigated varied by a factor of 5 and specific recommendations were given to keep this variation to a minimum.

© 2015 Published by Elsevier Ltd.

1. Introduction

Carbon capture and storage (CCS) is increasingly seen as a short term sustainable way for fulfilling the world energy needs while minimizing the environmental impact of fossil fuel combustion (Butt et al., 2012; IEA, 2012). Chemical-looping combustion (CLC) has arisen as a promising technology to carry out power production with CO₂ capture at lower energy penalty compared to other

CO₂ capture technologies, such as pre- and post-combustion technologies (Ekström et al., 2009). CLC is a combustion process which integrates power generation and CO₂ capture. It consists of two interconnected reactors, an air and a fuel reactor with a solid oxygen carrier circulating between them, thereby playing the role of oxygen transporter which transfers the oxygen required for fuel combustion from the air to the fuel. Consequently, any contact between the fuel and the air is inherently avoided in this process, and therefore a pure CO₂ stream, ready for compression and sequestration, after steam removal, is produced (Ishida et al., 1987).

In addition to development and selection of suitable oxygen carrier materials (hundreds of papers reported the development

* Corresponding author. Tel.: +47 46 639721.

E-mail address: shahriar.amini@sintef.no (S. Amini).

Fig. 1. Simple illustration of a GSC reactor. Air and fuel streams enter at room temperature and hot process gases are delivered to the downstream power cycle and CO_2 drying and compression unit.

of oxygen carriers for this process: e.g. (Johansson et al., 2006a,b; Zafar et al., 2006; Abad et al., 2007; Leion et al., 2008; Ryden et al., 2008; Shulman et al., 2009; Ryden et al., 2010; Adanez et al., 2012), research on CLC has so far been focused predominantly on the use of dual Circulating Fluidized Beds (CFBs) configuration for the recirculation of the oxygen carrier between the air and the fuel reactors (Ekström et al., 2009; Adanez et al., 2012). Although this configuration has been demonstrated experimentally at lab and pilot scales (Kronberger et al., 2004; Johansson et al., 2006a,b; Linderholm et al., 2008; Proell et al., 2009; Kolbitsch et al., 2010; Ding et al., 2012), the dual CFB-based CLC process is still facing many technical and operational complexities which arise mainly from the interconnected reactors configuration. Aside from the design and operational complexity created by the need to manage the solids exchange so that mass and heat balances within the closed loop are fulfilled, the exchange of solids itself brings additional costs and complexity. This circulation between the two reactors requires efficient and costly particles separation system such as a cyclone. This particle separation is particularly difficult due to the extremely harsh reactive and high temperature conditions. These challenges magnify under high pressure operation at which the CLC technology is more efficient compared with other capture technologies (Hamers et al., 2014).

Attempts have followed in recent years to address these issues where reactor concepts with no external solid circulation have been proposed (Noorman et al., 2007; Hakonsen and Blom 2011; Hamers et al., 2013; Zaabout et al., 2014a,b). The Gas Switching Combustion (GSC) concept which is the subject of this paper has been proposed as an alternative to the interconnected fluidized bed reactors used in the standard CLC process, where it uses a single fluidized bed reactor with alternating air and gaseous fuel feeds into the reactor (Fig. 1). External solids circulation is inherently avoided by the use of a switching mechanism which allows periodic feeding of fuel and

air streams to the single reactor where the oxygen carrier material undergoes redox reactions. The first experimental demonstration of this concept has been carried out using carbon monoxide (CO) as fuel (Zaabout et al., 2013). High CO_2 capture efficiency and CO_2 purity have been achieved by this process while maintaining simple operation and control of the process. This concept will bring other interesting benefits such as the ability of operation under high pressure conditions and ease of scale up.

As a clean combustion technology for power production, the ultimate purpose of the GSC is its integration in a natural gas fired power plant (NGCC) or in an Integrated gasification combined cycle power plant (IGCC). A recent process simulation study (Cloete et al., 2015) confirmed the GSC-IGCC concept as a promising concept for high-efficiency (up to 41.5%) baseload power-production with integrated CO_2 separation. As a first step towards the demonstration of the GSC concept, however, its behavior with syngas derived from solids fuel gasification and methane should be understood. This paper will therefore investigate the GSC concept flexibility to the fuel type. Specifically, methane and syngas are evaluated based on performance parameters such as CO_2 capture efficiency, CO_2 purity, carbon deposition and temperature rise. The experimental study will be followed by a thermodynamic analysis of the GSC reactor behavior with four oxygen carriers. Ultimately, the most suitable gaseous fuel for this concept will be identified.

2. Experiments and methods

2.1. Experimental set up

The experimental setup (Fig. 2) consisted of a pseudo-2D vertical column with a height of 1.5 m, a width of 0.3 m and a depth of 0.015 m. The pseudo-2D configuration was selected for the purpose of extracting local experimental data for detailed CFD model validation and was based on a cold flow unit with similar dimensions (Cloete et al., 2013). The reactor column was made from Inconel 600 in order to withstand the harsh conditions of high temperatures (up to 1000°C) and reacting gas–solid flows. A ceramic porous plate with 40 micron pores and 7 mm thickness was used as the gas distributor. A freeboard was added to the top to prevent particles losses. The setup was equipped with four electrical heaters (Thermcraft Inc.) installed on the back of the reactor in order to heat up the reactor to the target temperature (referred also as the operating temperature). Each of these heaters is controlled separately allowing for full control of the heat supply to the desired region in the reactor. Blanket insulation (25 cm thickness) was used to maintain the heat in the system.

Three mass flow controllers (Bronkhorst BV) were used for feeding gases to the reactor. The three gas lines gather at a three-way electrical valve installed before reaching the distributor. This three-way electrical valve is used to switch between feed gases. A cooler was positioned at the outlet of the reactor to cool down the stream of hot gases before it is sent to the vent.

The gas composition was measured using a Mass Spectrometer from MKS Instruments Inc. and the temperature was measured in each port along the entire front of the reactor using type K thermocouples. All the measurement instruments, flow controlling devices were controlled through a Labview application. The Labview application was also used for data acquisition and storage. Further details about the experimental setup can be found in (Zaabout et al., 2013, 2014a,b).

2.2. Operation

All GSC demonstration experiments reported in this paper were completed with an amount of oxygen carrier material corresponding to a 0.3 m static bed height in the reactor. Nickel oxide particles supported on Al_2O_3 (manufactured by VITO) were used as the

Fig. 2. Schematic representative of the experimental set up.

oxygen carrier. The NiO/Al₂O₃ ratio is 65/35 and the particle size cut-offs D10, D50 and D90 were determined to be 117.4, 161.7 and 231.3 μm respectively. About 37% of the final particle consists of free NiO which is available for reaction. The powder has a loosely packed density of 1950 kg/m³ and a tapped density of 2166 kg/m³. This oxygen carrier was selected because it has been successfully used in previous studies (Cho et al., 2004; Bolhar-Nordenkamp et al., 2009).

In autothermal operation, the reactor is first heated up externally to the target temperature before starting gas switching experiments. When heaters are switched off a pure gaseous fuel is fed for a fixed amount of time called as the “fuel time” to reduce the oxygen carrier and remove the heat which builds up from the highly exothermic oxidation reaction. Five seconds purging with pure N₂ is applied between the air and the fuel stages to avoid direct contact between fuel and air and thereby eliminate the risk of explosion.

Experiments were performed with three gaseous fuels with 4 min reduction time; CO was used for first testing of the reactor, then a detailed study with syngas and methane has followed. Constant gas feed of 45 Nl/min was applied for both reduction and oxidation stages. Various dependent variables were extracted from each experiment: the CO₂ purity, the CO₂ capture efficiency, the amount of carbon deposition, the maximum temperature variation and the oxidation/reduction time ratio (henceforth called the Oxi/Red time ratio). All dependent variables are averaged over the three complete redox cycles.

Throughout the study, all temperature measurements are taken at 0.3 m in the central axis of the reactor. Temperature variations at this point are followed throughout the experiment and used to determine the start and end of the redox cycles. Gas species measurements are taken at a height of 0.7 m which is a point in the freeboard well above the expanded bed. These measurements are used to determine the CO₂ purity and capture efficiency as well as the carbon deposition.

The pressure along the height of the reactor is measured regularly in order to quantify the bed weight and to inspect any unexpected loss of particles caused by elutriation of particles due to gas expansion when the reactor reaches higher temperatures.

It is worth mentioning that the GSC demonstration experiments are carried out at temperatures lower than those found in a real power plant where the GSC reactor will be integrated. This is for the sake of maintaining autothermal operation despite the large heat losses taking place in the experimental set up. Conclusions drawn from the low temperature demonstration experiments are valid for the operation of the GSC reactor under real power plant conditions.

2.3. Reactor performance

The performance of the GSC concept is assessed based on the quantification of the following dependent variables:

Fig. 3. Transient temperature at reactor heights of 0.02, 0.05 and 0.3 m over three redox cycles. CO was used as fuel at a target temperature of 700 °C. The blue region is the reduction stage and the pink region is the OXI stage.

- **CO₂ capture efficiency.** This was calculated by determining the percentage of the total produced CO₂ which exited in the outlet gas over the entire OXI stage (OXI will refer to oxidation and heat removal stage to avoid any confusion). The CO₂ capture efficiency was then taken as 100% minus the percentage of CO₂ that escaped to the atmosphere with the depleted air. Naturally, a high degree of CO₂ capture is desired in order to keep greenhouse gas emissions minimal.
- **CO₂ purity.** This was calculated by determining the amount of depleted air and unconverted gaseous fuel present in the outlet stream over the entire reduction stage. The CO₂ purity was then taken as 100% minus the percentage of impurities (depleted air and gaseous fuel) in the reduction stage outlet stream which would be sent to compression and storage in a real plant. Naturally, a high CO₂ purity is desired so that the volume of gas to be compressed, transported and stored is kept to a minimum.
- **Carbon deposition.** Carbon deposition reactions ($2\text{CO} \rightarrow \text{CO}_2 + \text{C}$ or $\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$) can occur on the Ni-based oxygen carrier (employed in this study) in the reduction stage to subsequently be combusted in the OXI stage and released to the atmosphere as CO₂. This is an undesired phenomenon and it was quantified as the molar ratio of the total amount of CO₂ released during the OXI stage and the total amount of CO/CH₄ fed to the reactor during the fuel stage. Carbon deposition was measured in a separate cycle where a long purging stage with nitrogen was applied after the reduction stage. This eliminated CO₂ leakage and ensured that all CO₂ measured during the subsequent OXI stage could be safely attributed to combustion of the deposited carbon.
- **Temperature rise.** Due to the transient cycling operation of the reactor, the reactor temperature will vary throughout the cycle (Fig. 3). It is important that this variation is not so large that lower temperatures cause incomplete fuel conversion or higher temperatures damage the reactor or downstream equipment. The difference between the maximum and minimum temperatures in the redox cycle will therefore be recorded in each experiment.
- **Oxi/Red time ratio.** With minor heat losses the OXI stage will be much longer than the fuel stage if constant flow rates are used. This is partially due to the molar density of oxygen in air which is lower than the molar density of the pure gaseous fuel, but primarily due to the large amount of heat must be removed from the system by the cold air after the oxygen carrier has been fully oxidized. The ratio between the OXI stage time and the reduction stage time will therefore be recorded for each experiment.

3. Results

Results will be presented and discussed as follows: first operation of the reactor has been carried out with CO as has been done

Fig. 4. Transient species mole fraction collected at a reactor height of 0.7 m over three redox cycles. CO was used as fuel at a target temperature of 700 °C. The blue region is the reduction stage and the pink region is the OXI stage.

previously in (Zaabout et al., 2013) to evaluate the reactor performance deviations from that found in (Zaabout et al., 2013) due to lower efficiency of the insulation material. Subsequently, a detailed study with syngas and methane at three target temperatures will be presented. Note that a mixture of hydrogen and carbon monoxide was used to simulate syngas (38% H₂ and 62% CO).

3.1. Carbon monoxide

In the ideal GSC process a target temperature is used as a threshold to switch from the OXI (oxidation and heat removal stages) to the reduction stage. A long heat removal stage using pure air follows the oxidation stage to remove heat built in the reactor due to the highly exothermic oxidation reaction. This mode of operation has been demonstrated in (Zaabout et al., 2013) where a good efficiency insulation system has been used.

In this study, experiments with CO as fuel have been carried out at a target temperature of 700 °C. This temperature is much lower than that which would be targeted in the real process (see Section 4) due to large heat losses from this lab-scale reactor. However, the process dynamics remains very similar to that which would be observed at real operating temperatures.

The external heaters were switched off after the reactor temperature reached 700 °C then periodic feeding with CO and air has followed for a number of redox cycles. Autothermal operation of the reactor has been achieved where the reactor temperature oscillated between minimal values reached at the start of the oxidation stage and maximal values reached at the end of the oxidation stage (Fig. 3). Complete CO conversion has been achieved.

In contrast to the previous study (Zaabout et al., 2013), no heat removal stage existed due to the substantial heat losses in the reactor. In order to maintain autothermal operation of the reactor, the switch to the reduction stage had to be made immediately when the temperature reaches the maximum. This switch occurred close to full oxidation of the oxygen carrier as can be observed from the transient oxygen mole fraction in the outlet gas stream approaching that of pure air as shown in Fig. 4. The cycle time is therefore much shorter and consequently a very low Oxi/Red time ratio and lower temperature rise has been found compared to that found in (Zaabout et al., 2013) despite the larger fuel feed (Table 1).

No carbon deposition was detected and CO₂ purity and capture efficiency remained high (94.5%). This confirms the GSC concept ability to maintain competitive capture performance in addition to the substantial reduction in the technical complexities found in the conventional interconnected reactors configuration.

Table 1

GSC performance parameters with carbon monoxide.

CO ₂ purity (%)	CO ₂ capture efficiency (%)	Oxi/Red time ratio	Temperature rise (°C)
94.5	94.5	2.45	24.98

3.2. Fuel sensitivity of the GSC concept

In industrial practice, natural gas and syngas (derived from gasification of coal or biomass) are the most important gases to consider for power production with the GSC concept via integration into an NGCC or IGCC power cycle. The following sections will therefore investigate and discuss the use of syngas and methane to fuel the GSC reactor.

In order to compensate for the large heat losses shown in the previous section, part of the heat losses will be compensated for via the external heaters. This will enable having longer redox cycle time, reaching the full oxidized state of the oxygen carrier and showing the existence of the heat removal stage which is an important component of the GSC concept. Yet even with the external heat supply the cycle time is still far away from the ideal one as will be shown in the mass and energy balance calculations presented in the next section. Experiments have been carried out for target temperatures of 600, 700 and 800 °C. The reactor performance with each gaseous fuel was evaluated based on the dependent variables as specified above (2.3).

3.2.1. Mass and energy balance

Mass and energy balance calculations are made first to predict the ideal performance of the GSC concept with syngas and methane at a target temperature of 700 °C. The ideal cycle time T_c can be calculated as specified by Eq. (1), where ΔH_c is the total heat of combustion, c_p is the mass specific heat capacity of the gas, ΔT is the gas temperature rise to reach the reactor temperature (note that the gas is fed at room temperature) and $\dot{m}_g$ is the gas mass flow rate. For the case of syngas, for 240 s feed at 45 Nl/min with the assumption of full conversion, a total heat of 2083.29 kJ is released in the reactor. Under the assumption of adiabatic operation, a total of 2.05 kg of gas is required to remove the heat released (the involved gases in the cycle are assumed to have the same specific heat capacity as air; 1.1 kJ/kg K). In standard conditions of pressure and temperature, 45 Nl/min gas feed corresponds to 0.00086 kg/s. Therefore the time required for complete heat removal (the cycle time) is 3280.11 s. The expected ideal Oxi/Red ratio is then 12.66.

In the case of methane, the feed rate is 1/4 of that used for syngas (this is because 1 mole of CH₄ reacts with 4 moles of NiO). The heat released for 240 s feed with methane is 1636.08 kJ. This will require lower amount of air for heat removal than in the case of syngas and therefore shorter time cycle. After all calculation made the ideal Oxi/Red time ratio for methane is 9.69.

As shown above, however, such a high ratio of the oxidation and reduction stage times cannot be achieved in the lab-scale reactor employed in this study because of substantial heat losses.

$$t_c = \frac{\Delta H_c}{c_p \Delta T \dot{m}_g} \quad (1)$$

Table 3

GSC performance parameters with methane.

Temperature (°C)	CH ₄ mole fraction	H ₂ mole fraction	CO mole fraction	CO ₂ purity	CO ₂ capture efficiency	Oxi/Red time ratio	Temperature rise
600	0.067	0.014	0.092	79.51	95.95	4.04	67.7
700	0.047	0.004	0.087	82.42	95.96	3.50	63.7
800	0.041	0.004	0.084	83.98	96.10	3.57	62.3

Table 2

GSC performance parameters with syngas.

Temperature (°C)	CO ₂ purity	CO ₂ capture efficiency	Oxi/Red time ratio	Temperature rise
600	95.7	97	4.6	64.9
700	95.2	96.4	4.1	54.6
800	94.9	95.6	3.9	53.9

Fig. 5. Transient species mole fraction collected at a reactor height of 0.7 m over three redox cycles. Syngas was used as fuel at a target temperature of 700 °C. The blue region is the reduction stage and the pink region is the OXI stage.

3.2.2. GSC with syngas

Complete syngas conversion has been achieved for the three operating temperatures. Consequently, high CO₂ purity values (95%) were achieved as shown in Table 2. When a complete fuel conversion is achieved, the only source of impurities in the reduction stage gas stream which could affect the CO₂ purity is the depleted air and nitrogen remaining in the reactor when switching to the reduction stage. No carbon deposition has been detected for the three operating temperatures, thereby leaving the CO₂ remaining in the reactor after the switch to air as the only source of impurities. This explains the high CO₂ capture efficiency reported in Table 2.

Fig. 5 shows the gas composition data collected at a reactor height of 0.7 m over three redox cycles. It can be clearly seen from the oxygen mole fraction that the oxygen carrier reaches a fully oxidized state and a heat removal stage follows before switching to the reduction stage. Oxi/Red time ratios around 4 were found. This is still only 30% of the expected ideal value predicted by the mass and energy balance despite the part of the heat losses compensated for externally. The observed decrease in the Oxi/Red time ratio with the operating temperature results from the larger heat losses and heat removed by the cold gas fed at higher temperature. The same reasons are behind the temperature rise decreases with the increase in the operating temperature.

3.2.3. GSC with methane

Operation with methane is found to be sensitive to the operating temperature. Incomplete methane conversion has been found for the three operating temperatures as can be seen in Table 3 although the conversion improves with higher temperatures. The transient methane mole fraction for a target temperature of 600 °C (Fig. 6) shows significant methane slip at the start of the reduction stage. Methane conversion then improves gradually towards complete

Fig. 6. Transient species mole fraction collected at a reactor height of 0.7 m over one redox cycle. Methane was used as fuel at a target temperature of 600 °C. The blue region is the reduction stage and the pink region is the OXI stage.

conversion at the end of the reduction stage. A corresponding high percentage of carbon monoxide was also found at the start of the reduction stage and decreases following the same trend as methane toward full conversion at the end of the reduction stage.

The methane and carbon monoxide mole fraction trends can be explained by considering the prevailing reactions between methane and Ni/NiO (a good overview can be found in (Zhou et al., 2013)): At the start of the reduction stage methane conversion is low because it splits first to carbon monoxide and hydrogen through the steam methane reforming (SMR) reaction (Eq. (2)). SMR is catalyzed by metallic nickel and is therefore low at the start of the reduction stage when the oxygen carrier is highly oxidized (Medrano et al., 2014), leading to incomplete methane conversion (the only reaction occurring at this stage is the gas/solid reaction of methane and oxygen carrier to reduce the NiO to Ni). As soon as a small amount of Ni is present, the steam reforming reaction starts and hydrogen is therefore produced along with CO and CO₂. The highly reactive H₂ produced by the SMR reaction then reacts to completion with the abundant NiO available (reducing it to Ni), but the less reactive CO shows some degree of fuel slip. However, as more NiO is reduced to Ni, both the SMR and water-gas shift (WGS, Eq. (3)) reactions become faster. Increases in the SMR reaction improve methane conversion, while increases in the WGS reaction improve CO conversion to more reactive H₂. The continuous combustion of H₂ via the heterogeneous reaction with NiO continuously drives both these equilibrium reactions towards the right, thereby producing more H₂ and leading to improved overall conversion. When the oxygen carrier reaches a highly reduced state, hydrogen mole fraction in the gas stream increases due to the lack of oxygen (from NiO) leading to some H₂ slip. Higher operating temperatures however prolong the complete conversion of the produced hydrogen which leads to further conversion of carbon monoxide and methane. This explains the complete conversion of hydrogen observed for 700 and 800 °C (Table 3), over the whole reduction stage.

Incomplete methane conversion over Ni-based oxygen carriers supported on Al₂O₃ at the start of the reduction phase has been reported in other studies under fluidized and packed bed conditions (Jerndal et al., 2009; Iliuta et al., 2010). Addition of 5 wt% MgO or the use of MgAl₂O₄ as a support has been shown to result in excellent methane conversion.

The incomplete conversion of methane and existence of uncombusted carbon monoxide reduces greatly the CO₂ purity when methane is used as a reducing gas. CO₂ purity in the range of 80% was found for 600 °C, with slight improvements when increasing the operating temperature to 800 °C. Otherwise, other oxygen carriers which favor direct methane combustion should be used.

The CO₂ capture efficiency is however maintained at a high level due to the absence of carbon deposition (Table 3). As mentioned above this parameter is only affected by the CO₂ leakage when switching to the oxidation phase.

Operation with methane exhibits higher temperature rise than syngas. This is attributed to the endothermic reaction of methane with nickel oxide oxygen carrier while syngas reaction with nickel oxide is slightly exothermic. Methane also results in lower decrease rate in the temperature rise than syngas. The improvement in methane conversion with the increase in the operating temperature results in further heat release in the reactor and compensates for the increased heat losses and heat removal by the cold gas feed. As for the Oxi/Red time ratio, values between 3.5 and 4 were found. This is still less than 40% the expected ideal values despite the external heaters.

4. Thermodynamic analysis with different oxygen carriers

This section will assess the behavior of the GSC concept with different oxygen carriers. The emphasis falls on the estimation of the temperature variation within the cycle as minimization of this parameter is an important consideration for integration with a downstream power generation cycle (Cloete et al., 2015). Firstly, gasses should enter the power cycle as close as possible to the maximum operating temperature of the process to ensure high electric efficiency. Larger temperature variations across the cycle imply that the average outlet temperature of the reactor will reduce. Secondly, large temperature variations can cause increased turbine wear, even if outlet streams of different reactors are combined.

Section 3.2 illustrated how the fuel type used can influence the temperature variation across the cycle as a result of the different thermodynamic properties of the fuel gasses. This section will extend this philosophy to different oxygen carrier types in order to explore the potential of temperature variation minimization through intelligent material selection.

In this investigation, three typical temperatures marking transitions between the different stages in the redox cycle will be determined for the different oxygen carriers and fuels. These three temperatures are respectively: temperature at the start of the reduction stage (TSR), temperature at the start of the oxidation stage (TSO) and temperature at the end of the oxidation stage (TEO). The temperature at the end of the oxidation (TEO) will be referred to as the targeted temperature representing the maximum safe reactor operating temperature.

These three temperatures will be calculated for four oxygen carriers: Ni/NiO, Fe₂O₃/Fe₃O₄, ilmenite and MnO/Mn₃O₄. The two first oxygen carriers are supported on Al₂O₃ (those oxygen carriers are the same used for theoretical calculations for a CLC system in (Abad et al., 2007)). Ilmenite is mainly composed of TiO₂, playing the role of the inert material, and Fe₂O₃/FeO as the active material (Abad et al., 2011). The Manganese based oxygen carrier used in this study is supported on CeO₂ (Bhavsar et al., 2014).

Mass and heat balances (Eqs. (4) and (5)) were solved for each combination of oxygen carrier and fuel in order to calculate the temperature variation across the cycle. Temperature dependent specific heat capacities were used in the calculations according to data provided in (Robie and Hemingway, 1995). A fixed energy content of fuel and mass of oxygen carrier (assumed to be the mass that would result in complete conversion of the Fe₂O₃/Fe₃O₄ material which had the lowest oxygen carrying capacity) was employed in

Fig. 7. Temperature variation for the different oxygen carriers at different targeted temperatures. 1 MJ of methane was used as fuel and a constant mass of 5308 g was used for each oxygen carrier.

all cases. Three different targeted temperatures (TEO) were investigated: 1273 K, 1373 K and 1473 K.

$$\int_{TSR}^{TSO} m_s C_{Ps}(T) dT + \int_{298}^{(TSO+TSR)/2} m_g C_{Pg}(T) dT = \Delta H_{red} \quad (4)$$

$$\int_{TSO}^{TEO} m_s C_{Ps}(T) dT + \int_{298}^{(TEO+TSO)/2} m_g C_{Pg}(T) dT = \Delta H_{oxi} \quad (5)$$

4.1. Reduction with methane

The temperature variation across the cycle for reaction of a fixed mass of the different oxygen carriers with a fixed amount of methane is given in Fig. 7 for the three targeted temperatures. It is clear that the temperature variation decreases with increasing targeted temperature. This is due to two factors: (1) the general increase in material heat capacity with temperature and (2) the increasing amount of heat extracted by the fluidizing air limiting the temperature rise under oxidation with increasing bed temperature.

Fig. 7 also shows large differences between the different oxygen carriers. These differences can primarily be explained by the differences in reaction enthalpy, but differences in heat capacity also play a role. To better illustrate this point, the MnO/Mn₃O₄ material, which is the only material with an exothermic reduction reaction with methane, is presented both with the standard CeO₂ support and with an Al₂O₃ support which has a much higher heat capacity. It is clear that the higher heat capacity support greatly reduces the temperature rise, while the exothermic reduction reaction limits the temperature rise when the low heat capacity support is used.

The advantageous effect of the exothermic reduction reactions of MnO/Mn₃O₄ is clearly visible in Fig. 8 (small difference between TSR and TSO). It is clear, however, that the low heat capacity of the CeO₂ support negates most of the advantage that the exothermic reduction of Mn₃O₄ brings (large difference between TSO and TEO). A high heat capacity support therefore appears to be essential for making the MnO/Mn₃O₄ highly applicable to the GSC process.

4.2. Comparison of methane and syngas

The behavior of the GSC reactor with syngas was also investigated using the composition specified in Table 4. The relative performance of the different oxygen carrier materials with syngas is found similar to that shown for reduction with methane in

Fig. 8. Temperatures at the start of the reduction (TSR), start of oxidation (TSO) and end of oxidation (TEO), for a targeted temperature of 1473 K for the different oxygen carriers. 1 MJ of methane was used as fuel and a constant mass of 5308 g was used for the four oxygen carriers.

Table 4

Syngas composition.

Syngas	x (vol)
CO	0.335
CO ₂	0.317
H ₂	0.143
H ₂ O	0.182
N ₂	0.023

Fig. 9. Comparison of the temperature rise exhibited by methane and syngas for the different oxygen carriers. 1 MJ of fuel and 5308 g of oxygen carrier were used with a targeted temperature of 1473 K.

Fig. 7: the temperature variation decreases with increasing targeted temperature

When compared to methane, syngas exhibits relatively smaller temperature variations in the redox cycle (as also observed in Section 3.2). This is simply due to the fact that more energy is released in the reduction stage when reducing with syngas as opposed to methane. As outlined in the previous section, more heat release in the reduction stage is beneficial to the process by limiting the temperature variation across the cycle. This improved performance relative to methane is shown directly in Fig. 9.

4.3. Discussion

The previous two sections have identified four important factors that can be employed to limit the temperature variation across the GSC cycle carried out with a fixed amount of fuel energy and oxygen carrier mass: (1) the heat of formation of the active oxygen carrier components, (2) the heat capacity of the oxygen carrier material, (3) the heat of combustion of the fuel and (4) the maximum process

temperature. As a result of changing these factors, the temperature variation across the cycle could be varied over a factor of five.

Regarding point 1, materials that release heat under reduction are the most promising. In this study, Mn-based materials fulfilled this criterion. Point 2 was also shown to have a large effect and can be manipulated by selection of the support material (Fig. 9). For point 3, Fig. 9 clearly shows that syngas results in lower temperature variations across the cycle than methane. With regard to point 4, the results in Fig. 7 confirm that increases in reactor temperature also serve to limit the temperature variation across the cycle.

These results can be used to identify the best conditions for high-efficiency GSC operation. Firstly, the active oxygen carrier component must be selected to exhibit exothermic reduction and also to withstand elevated temperatures. Mn-based materials appear to be the most promising candidates according these criteria. Secondly, it is important that the heat capacity of the system be maximized. Alumina support materials appear to be highly beneficial in this regard, but was rejected in previous study because of the formation of highly irreversible and unreactive phase (Adanez et al., 2012). Further research is therefore required to find a high heat capacity support for Mn-based materials. It is also theoretically possible to substantially increase the heat capacity of the reactor itself via the inclusion of some fixed metal rods within the bed to further limit the temperature variation across the cycle. Lastly, the use of syngas fuel, preferably with a high CO content will further reduce the temperature variation across the cycle.

Even though more thorough investigations are required to quantify the impact of these measures on plant efficiency, previous results suggest that a factor of 5 reduction in the temperature variation across the cycle can improve the electric efficiency by about 10% (on a relative basis (Cloete et al., 2015)). It is therefore clear that reductions in the temperature variation across the cycle can result in significant efficiency improvements which would make the GSC concept substantially more attractive.

In closing, it should be noted that other challenges related to the integration of the GSC reactor in a combined cycle could be anticipated. The primary technical uncertainty introduced by this configuration is the need for a high temperature ($\sim 1200^\circ\text{C}$) valve system to regulate the reactor outlet streams. Fines generation is also a second important general challenge when using high pressure fluidized beds for power production integrated in a combined cycle due to the need for high temperature filtering systems for protecting the gas turbine. More work is required to assess the magnitude of these challenges.

5. Conclusion

Further experimental demonstration of the gas switching combustion (GSC) concept has been carried out in this paper, followed by an analysis of the temperature variation across the GSC cycle with different oxygen carriers and methane and syngas as fuels. This concept has been proposed as an alternative of the conventional chemical looping combustion (CLC) process for power production with integrated CO_2 capture which uses interconnected fluidized bed reactors. In the GSC concept, a single fluidized bed reactor is used with alternating air and fuel gas feeds into a bed of oxygen carrier in the same reactor. This completely avoids any need for oxygen carrier circulation and thereby avoids many technical and scale-up challenges related to the looping concept.

After a previous successful demonstration of the GSC concept where it was shown that the reactor could operate autothermally to continuously convert cold feed gases into hot product gases, the GSC concept was further tested in this paper with other fuel gases of more commercial interest for power generation (syngas and methane). Experiments with syngas (62% CO and 38% H_2) and

methane were carried out using the same Ni-based oxygen carrier as in the previous study. Partial external heat supply has been applied in order to compensate for part of heat losses and show the heat removal stage with these fuel gases.

Syngas showed complete conversion with no carbon deposition, thereby leading to high CO_2 purity (95%) and capture efficiency (95%). Incomplete methane conversion was however found together with existence of carbon monoxide in the gas stream. The transient gas composition measured in the freeboard showed a higher percentage of unconverted methane at the start of the reduction stage which improves toward full conversion at the end of the reduction stage. Gas composition data also showed the existence of large amount of carbon monoxide at the start of the reduction stage and which follows the same trend as methane where it reaches close to complete conversion at the end of the reduction stage. The existence of unconverted methane and carbon monoxide greatly reduces the CO_2 purity of the GSC concept where values around 80% were found. Increasing the operating temperature slightly enhanced methane conversion but improvement in CO_2 purity remained below expectations. High CO_2 capture efficiency (95%) has however been achieved due to the absence of carbon deposition.

The thermodynamic calculations have identified the most important factors influencing the temperature variation across the GSC cycle. These factors can be used to control the temperature variation over a range spanning a factor of 5 and thereby maximize the electric efficiency of the down-stream power cycle. The oxygen carrier and fuel types were the most important parameters influencing the temperature variation, but the target temperature of the process and the heat capacity of the oxygen carrier were also proven to have significant influences.

In the light of its excellent performance, both in terms of high conversion and low temperature variation, syngas is suitable to fuel the GSC reactor. A syngas fuelled GSC reactor cluster would be deployed in a baseload integrated gasification combined cycle (IGCC) plant where its relative simplicity regarding design, scaling and pressurization could lead to a cost effective solution relative to alternative technologies. Such a plant would perform best with a Mn-based oxygen carrier supported on a material with a high heat capacity in order to further limit the temperature variation.

Methane could also be potentially used as fuel for the GSC concept if the issue of the slow reactivity at the start of the reduction stage is solved by means of oxygen carriers with low catalytic activity for the steam methane reforming reaction. Even though methane showed greater temperature variations across the cycle than syngas, this variation can still be minimized by good oxygen carrier selection and high temperature operation.

Acknowledgements

The authors would like to acknowledge the funding received from the Research Council of Norway which enabled the completion of this work under the project FLOW@CLC. Joost Kors is acknowledged for constructing and maintaining the experimental setup. Paul Hamers is acknowledged for his technical support with the Mass Spectrometer.

References

- Abad, A., Adánez, J., Cuadrat, A., García-Labiano, F., Gayán de Diego, P.L.F., 2011. Kinetics of redox reactions of ilmenite for chemical-looping combustion. *Chem. Eng. Sci.* 66 (4), 689–702.
- Abad, A., Adánez, J., García-Labiano, F., de Diego, L.F., Gayán, P., Celaya, J., 2007. Mapping of the range of operational conditions for Cu-, Fe-, and Ni-based oxygen carriers in chemical-looping combustion. *Chem. Eng. Sci.* 62 (1–2), 533–549.

- Adanez, J., Abad, A., Garcia-Labiano, F., Gayan, P., de Diego, L.F., 2012. Progress in chemical-looping combustion and reforming technologies. *Prog. Energy Comb. Sci.* 38 (2), 215–282.
- Bhavsar, S., Tackett, B., Vesar, G., 2014. Evaluation of iron- and manganese-based mono- and mixed-metallic oxygen carriers for chemical looping combustion. *Fuel* 136, 268–279.
- Bolhar-Nordenkamp, J., Proll, T., Kolbitsch, P., Hofbauer, H., 2009. Performance of a NiO-based oxygen carrier for chemical looping combustion and reforming in a 120 kW unit. In: Gale, J., Herzog, H., Braitsch, J. (Eds.), *Greenhouse Gas Control Technol.* 9 (1), 19–25.
- Butt, T.E., Giddings, R.D., Jones, K.G., 2012. Environmental sustainability and climate change mitigation-CCS technology, better having it than not having it at all. *Environ. Prog. Sustainable Energy* 31 (4), 642–649.
- Cho, P., Mattisson, T., Lyngfelt, A., 2004. Comparison of iron-, nickel-, copper- and manganese-based oxygen carriers for chemical-looping combustion. *Fuel* 83 (9), 1215–1225.
- Cloete, S., Zaabout, A., Johansen, S.T., v. Annaland, M.S., Gallucci, F., Amini, S., 2013. The generality of the standard 2D TFM approach in predicting bubbling fluidized bed hydrodynamics. *Powder Technol.* 235, 735–746.
- Cloete, S., Zaabout, A., Romano, M.C., Chiesa, P., Lozza, G., Gallucci, F., v. Annaland, M.S., Amini, S., 2015. Heat management in gas switching combustion for power production with integrated CO₂ capture. In: *The 7th International Conference on Applied Energy-ICAEE2015, Abu Dhabi, United Arab Emirates*.
- Ding, N., Wang, Y., Luo, C., Fu, P.F., Zheng, C.G., 2012. Development and testing of an interconnected fluidized-bed system for chemical looping combustion. *Chem. Eng. Technol.* 35 (3), 532–538.
- Ekström, C., Schwendig, F., Biede, O., Franco, F., Haupt, G., de Koeijer, G., Papapavlou, C., Røkke, P.E., 2009. Techno-economic evaluations and benchmarking of pre-combustion CO₂ capture and oxy-fuel processes developed in the European ENCAP project. *Energy Procedia* 1 (1), 4233–4240.
- Hakonsen, S.F., Blom, R., 2011. Chemical looping combustion in a rotating bed reactor—finding optimal process conditions for prototype reactor. *Environ. Sci. Technol.* 45 (22), 9619–9626.
- Hamers, H.P., Gallucci, F., Cobden, P.D., Kimball, E., van Sint Annaland, M., 2013. A novel reactor configuration for packed bed chemical-looping combustion of syngas. *Int. J. Greenhouse Gas Control* 16, 1–12.
- Hamers, H.P., Romano, M.C., Spallina, V., Chiesa, P., Gallucci, F., v. Annaland, M.S., 2014. Comparison on process efficiency for CLC of syngas operated in packed bed and fluidized bed reactors. *Int. J. Greenhouse Gas Control* 28, 65–78.
- IEA, 2012. *World Energy Outlook 2012*. International Energy Agency.
- Iliuta, I., Tahoces, R., Patience, G.S., Riffart, S., Luck, F., 2010. Chemical-looping combustion process: kinetics and mathematical modeling. *AIChE J.* 56 (4), 1063–1079.
- Ishida, M., Zheng, D., Akehata, T., 1987. Evaluation of a chemical-looping-combustion power-generation system by graphic exergy analysis. *Energy* 12 (2), 147–154.
- Jerndal, E., Mattisson, T., Lyngfelt, A., 2009. Investigation of different NiO/NiAl₂O₄ particles as oxygen carriers for chemical-looping combustion. *Energy Fuels* 23 (1), 665–676.
- Johansson, E., Mattisson, T., Lyngfelt, A., Thunman, H., 2006a. A 300 W laboratory reactor system for chemical-looping combustion with particle circulation. *Fuel* 85 (10–11), 1428–1438.
- Johansson, M., Mattisson, T., Lyngfelt, A., 2006b. Investigation of Mn₃O₄ with stabilized ZrO₂ for chemical-looping combustion. *Chem. Eng. Res. Des.* 84 (A9), 807–818.
- Kolbitsch, P., Bolhar-Nordenkamp, J., Proell, T., Hofbauer, H., 2010. Operating experience with chemical looping combustion in a 120 kW dual circulating fluidized bed (DCFB) unit. *Int. J. Greenhouse Gas Control* 4 (2), 180–185.
- Kronberger, B., Johansson, G., Mattisson, T., Lyngfelt, A., Hofbauer, H., 2004. A two-compartment fluidized bed reactor for CO₂ capture by chemical-looping combustion. *Chem. Eng. Technol.* 27 (12), 1318–1326.
- Leion, H., Lyngfelt, A., Johansson, M., Jerndal, E., Mattisson, T., 2008. The use of ilmenite as an oxygen carrier in chemical-looping combustion. *Chem. Eng. Res. Des.* 86 (9A), 1017–1026.
- Linderholm, C., Abad, A., Mattisson, T., Lyngfelt, A., 2008. 160 h of chemical-looping combustion in a 10 kW reactor system with a NiO-based oxygen carrier. *Int. J. Greenhouse Gas Control* 2 (4), 520–530.
- Medrano, J.A., Hamers, P., Ortiz, M., Ramirez, A., Annaland, M.v.S., Williams, G., Gallucci, F., 2014. NiO/CaAl₂O₄ as active oxygen carrier for low temperature chemical looping applications. In: *3rd International Conference on Chemical Looping, Göteborg, Sweden*.
- Noorman, S., Annaland, M., van Sint, Kuipers, 2007. Packed bed reactor technology for chemical-looping combustion. *Ind. Eng. Chem. Res.* 46 (12), 4212–4220.
- Proell, T., Kolbitsch, P., Bolhar-Nordenkamp, J., Hofbauer, H., 2009. A novel dual circulating fluidized bed system for chemical looping processes. *AIChE J.* 55 (12), 3255–3266.
- Robie, R.A., Hemingway, B.S., 1995. *Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 bar Pressure and at Higher Temperatures*. Geological Survey Bulletin, Washington, U.S., pp. 2131.
- Ryden, M., Cleverstam, E., Johansson, M., Lyngfelt, A., Mattisson, T., 2010. Fe₂O₃ on Ce-, Ca-, or Mg-stabilized ZrO₂ as oxygen carrier for chemical-looping combustion using NiO as additive. *AIChE J.* 56 (8), 2211–2220.
- Ryden, M., Lyngfelt, A., Mattisson, T., Chen, D., Holmen, A., Bjorgum, E., 2008. Novel oxygen-carrier materials for chemical-looping combustion and chemical-looping reforming: La_{0.8}Sr_{0.2}Fe_{0.8}Co_{0.2}O_{3-δ} perovskites and mixed-metal oxides of NiO, Fe₂O₃ and Mn₃O₄. *Int. J. Greenhouse Gas Control* 2 (1), 21–36.
- Shulman, A., Linderholm, C., Mattisson, T., Lyngfelt, A., 2009. High reactivity and mechanical durability of NiO/NiAl₂O₄ and NiO/NiAl₂O₄/MgAl₂O₄ oxygen carrier particles used for more than 1000 in a 10 kW CLC reactor. *Ind. Eng. Chem. Res.* 48 (15), 7400–7405.
- Zaabout, A., Cloete, S., Amini, S., 2014a. Hydrodynamic investigation into a novel IC-CLC reactor concept for power production with integrated CO₂ capture. In: *10th International Conference on Computational Fluid Dynamics in the Oil & Gas Metallurgical and Process Industries, Trondheim, Norway*.
- Zaabout, A., Cloete, S., Johansen, S.T., Annaland, M.v.S., Gallucci, F., Amini, S., 2013. experimental demonstration of a novel gas switching combustion reactor for power production with integrated CO₂ capture. *Ind. Eng. Chem. Res.* 52 (39), 14241–14250.
- Zaabout, A., Cloete, S., Amini, S., 2014b. Operating experience with a high-temperature pseudo-2D fluidized bed reactor designed especially for detailed local data collection. In: *10th International Conference on Computational Fluid Dynamics in the Oil & Gas Metallurgical and Process Industries, Trondheim, Norway*.
- Zafar, Q., Mattisson, T., Gevert, B., 2006. Redox investigation of some oxides of transition-state metals Ni, Cu, Fe, and Mn supported on SiO₂ and MgAl₂O₄. *Energy Fuels* 20 (1), 34–44.
- Zhou, Z., Han, L., Bollas, G.M., 2013. Model-based analysis of bench-scale fixed-bed units for chemical-looping combustion. *Chem. Eng. J.* 233, 331–348.