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Project acronym: GaSTech

Project title: Demonstration of Gas Switching Technology for Accelerated Scale-up of Pressurized Chemical Looping Applications (GaSTech)

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Duration: 18 months

WP N°	Del/ Mil N°	Title	Contributors	Version	Lead beneficiary	Nature	Dissemin. level*	Delivery date from contract dd/mm/yyyy	Actual delivery date 02/02/2021
2	2.2	GSR demonstration	SINTEF		NTNU	Report	PU	30/06/2018	10/12/2018

***Dissemination Level**		
PU	Public	X
PP	Restricted to other programme participants (including the Commission Services)	
RE	Restricted to a group specified by the consortium (including the Commission Services)	
CO	Confidential, only for members of the consortium (including the Commission Services)	

1 Introduction

Activities of task 2.2 "Demonstration of Gas Switching Reforming (GSR) pressurized operation" were completed. Chemical looping reforming (CLR) is a process for the production of syngas (CO + H_2) with inherent CO_2 capture [1]. In the conventional CLR, the oxygen carrier circulates between two interconnected fluidized-bed reactors (fuel and air reactor) (*Figure 1*a). The metal oxide acts as both oxygen carrier and catalyst and is first reduced to metallic radical which catalyzes the reforming reaction between CH_4, H_2O, and/or CO_2 to produce syngas. Ni-based metal oxides are commonly used due to their high catalytic activity for methane reforming [2, 3]. Although reforming reactions in the fuel stage is highly endothermic, CLR process could be integrated to utilize the heat from the exothermic oxidation reaction in the air stage to reduce the energy penalty and achieve autothermal operation [4].

In this work the chemical looping reforming is operated under the GST (single fluidized bed reactor without external solid circulation) called Gas Switching Reforming (GSR). This includes both the steam and dry methane reforming (*Figure 1*b and *Figure 2*b). Experiments were completed in the set up shown in *Figure 2*. Real time temperature and gas composition (using an ETG Syngas analyzer) were measured. The experiments were conducted at bubbling regime to ensure good heat transfer.

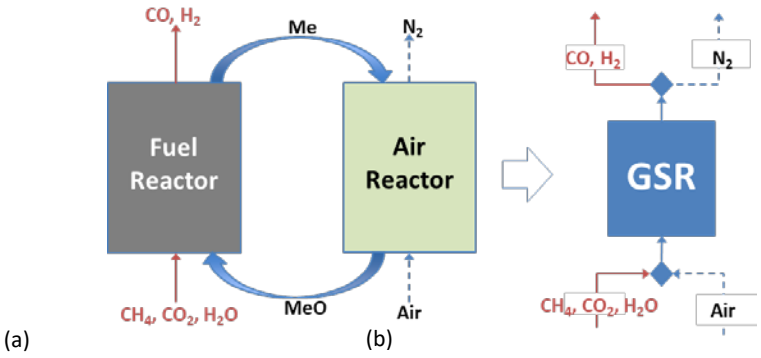

Figure 1: (a) Configuration of the convention Chemical Looping Reforming and (b) novel Gas Switching Reforming.

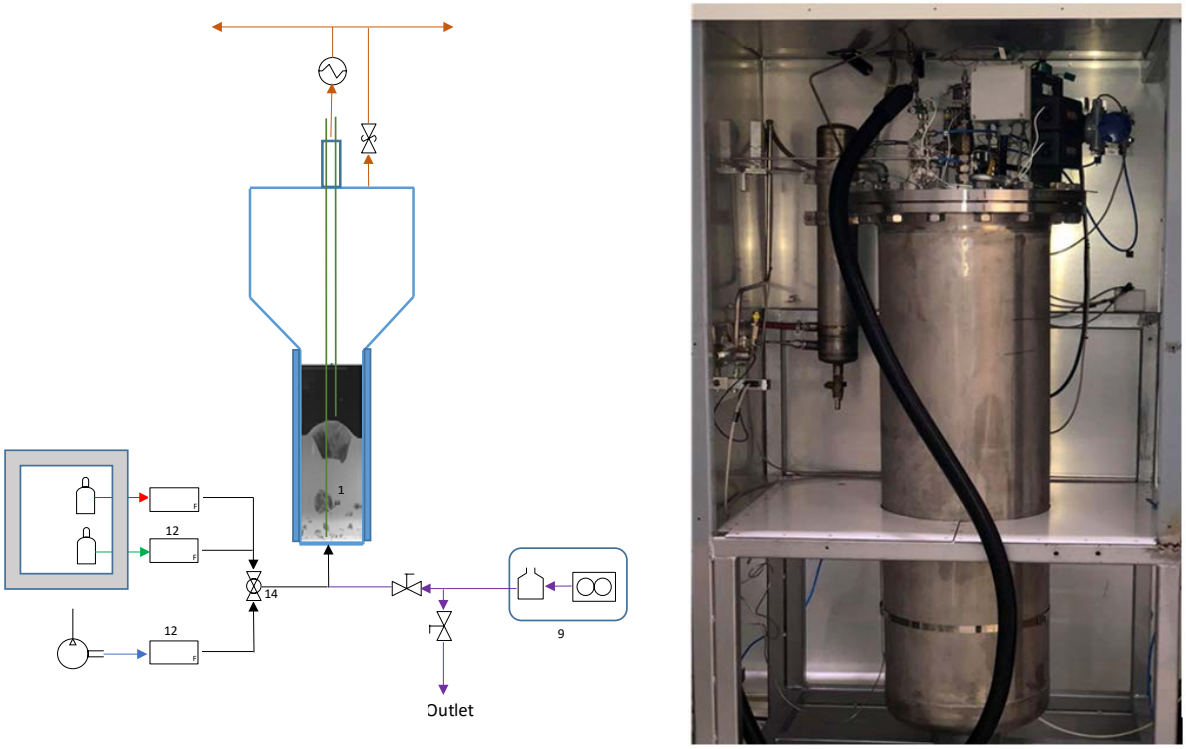

Figure 2: The GST reactor setup.

2 Results

2.1 Steam methane reforming

GSR has been experimentally demonstrated using Ni-based catalysts at 1 bar [5]. However, there is still a need for further demonstration at pressurized conditions with the possibility of a non-Ni-based oxygen carrier for scale-up and commercialization of this concept.

An iron-based oxygen carrier with high iron content (70%Fe_2O_3 + 30%Spinel), was tested under GSR conditions at atmospheric pressure in the existing 5 cm ID reactor (*Figure 4*). This is to explore Ni-free operation of the GSR concept. Selected results are shown in *Figure 3*. Activation of the oxygen carrier was first applied through short redox cycles using air and dry methane, before staring GSR cycles. It can be seen for the regular long cycles that CO concentration goes down while hydrogen increases highlighting the same challenges associated with this oxygen carrier as reported in the deliverable report D2.1. This was due to the substantial carbon deposition which wasn't solved even co-feeding steam with methane. Interestingly, in contrast to the case of the GSWS concept, no particle agglomeration has occurred in GSR. The main reason is that no high reduction level of the oxygen carrier is required in GSR to start methane reforming to syngas in the presence of steam. Nevertheless, the high carbon deposition makes such oxygen carrier with a high iron content not suitable for this process.

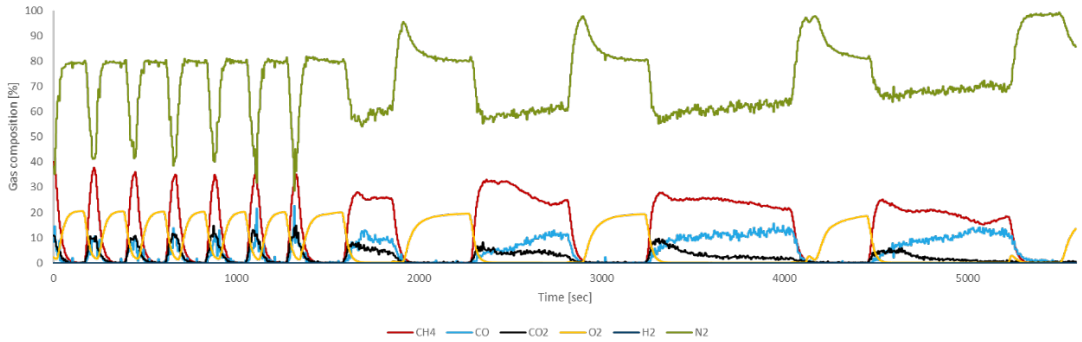

Figure 3: reactor performance with the 75% iron loading oxygen carrier: First 6 cycles: activation with shorth redox cycles (CH_4-5nl/min for 1min, Air-10nl/min – 2min). In the additional cycles steam was co-fed with methane in the fuel stage to complete the GSR cycle.

2.2 Dry methane reforming

The working principle of Gas Switching Dry Reforming (GSDR) is very similar to the Gas Switching Reforming (GSR) demonstrated earlier for syngas production with integrated CO_2 capture [6, 7]. It is a three-stage process as illustrated in *Figure 4* comprising of a **fuel stage** where the oxygen carrier is reduced to metallic radical to catalyze the endothermic dry reforming reaction at the consecutive **reforming stage**. The third stage is the **air stage** where the oxygen carrier is reoxidized to generate the heat needed for the highly endothermic dry reforming reaction.

To demonstrate autothermal operation of the GSDR process, part of the CO produced during the reforming stage is used as fuel in the reduction stage to sustain the bed temperature since the reduction reaction of NiO with CO is slightly exothermic. The separate reduction stage of GSDR will especially be beneficial if the GSDR is integrated with a Gas-To-Liquid (GTL) process, allowing the unconverted GTL outlet gases to be fed to the reduction stage of GSDR, thereby maximizing fuel usage and overall process efficiency.

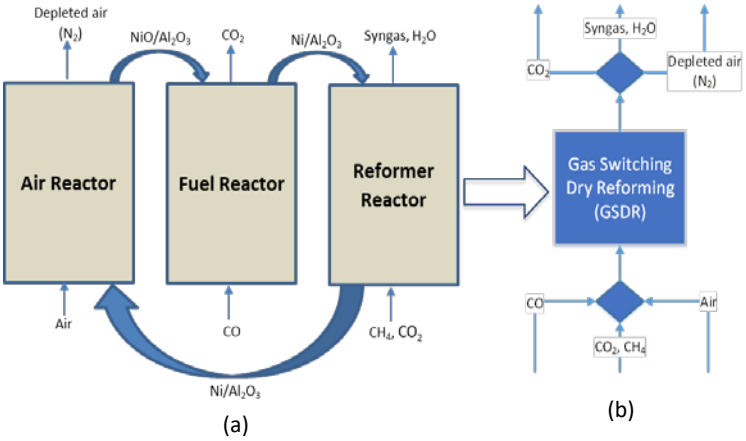

Figure 4: Conceptual schemes of dry reforming process. (a): completed following the chemical looping route. (b): Gas Switching Dry Reforming, GSDR.

Gas switching dry reforming was demonstrated using Ni-based carrier in a three-stages process (*Figure 5*a) under autothermal and pressurized operation. The ability to control the syngas quality (H_2:CO ratio) was demonstrated by adjusting CO_2:CH_4 ratio and addition of steam. The H_2/CO molar ratio between 0.25 – 2 was achieved with up to 90% syngas purity suitable for different GTL (gas-to-liquid) processes. Integrating GSDR to GTL processes can achieve improved process efficiency, reduced GHG emission and increased profitability. It is interesting to mention that when the CO_2:CH_4 ratio was increased beyond 2, carbon deposition was completely avoided. By co-feeding, steam, CO_2 and CH_4, the

combined effects of steam methane reforming and dry methane reforming was achieved with the following benefits: i) desirable syngas quality (H_2/CO molar ratio) between 1 – 3 suitable for GTL processes, ii) reduced carbon deposition and iii) reduced cost by the elimination of air separation unit used in the conventional tri-reforming/autothermal reforming alternatives. The successful high-pressure demonstration has proven the viability of the GSDR integration to downstream pressurized GTL processes. Although other previous studies have shown no negative effect of pressure on the kinetics of the dry reforming reaction, the gas conversion to syngas of the GSDR process was affected negatively by pressure.

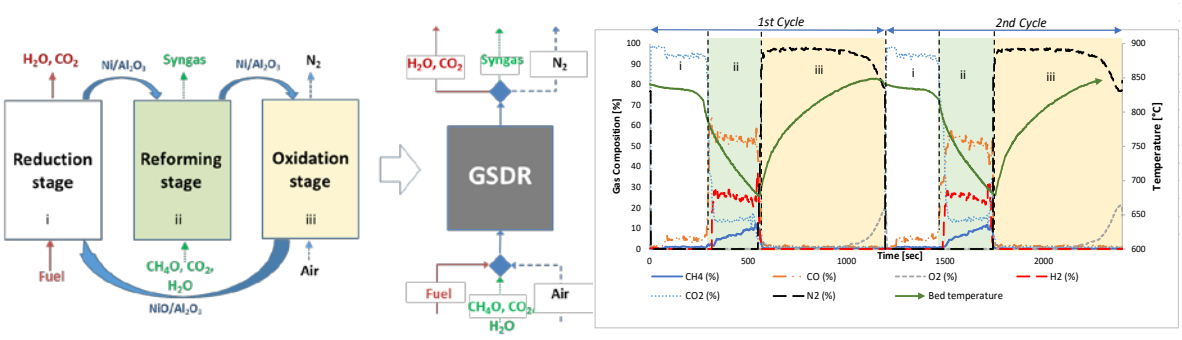

Figure 5: (Left)The three-stage Gas switching dry reforming process design, (Right) Two autothermal GSDR cycles showing transient gas composition and temperature profile. The reduction starts at a temperature of 850°C (target temperature). 1bar operating pressure, CO_2/CH_4 molar ratio of 2 and gas flowrate as follows; CO- 12.8nl/min, CH_4- 3.2nl/min, CO_2-6.4nl/min, Air- 10nl/min. i, ii and iii represent the reduction, reforming and oxidation stages respectively.

3 Conclusion

First GSR experiments were completed in the existing 5 cm reactor at SINTEF/NTNU, using the 70% Fe_2O_3 loading oxygen carrier developed earlier within the project for the GSWS. Acceptable methane conversion was achieved in the reforming stage producing syngas. In contrast to the case of the GSWS concept, no particle agglomeration has occurred in GSR. The main reason is that no high reduction level of the oxygen carrier is required in GSR to start methane reforming to syngas in the presence of steam as revealed in a previous study with an iron-based oxygen carrier. The high carbon deposition makes this oxygen carrier unsuitable for GSR.

Further demonstration was completed on the utilization of CO_2 in dry reforming of methane to produce syngas for GTL applications using Ni-based oxygen. Autothermal and pressurized operations were achieved with the ability to control the syngas ratio (H_2:CO) by adjusting CO_2:CH_4 ratio and addition of steam. By varying the CO_2:CH_4 ratio from 0.25 – 2, the desired H_2/CO molar ratio between 1-3 was achieved with up to 90% syngas purity suitable for GTL processes. Although carbon deposition was significant for the cases with CO_2:CH_4 ratio less than 2, the activity and catalyst stability were not negatively affected since the cyclic nature of GSDR ensured that all the produced carbon was gasified/combusted in the preceding reforming and oxidation stages.

References

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