Project ID: 271511

Project acronym: GaSTech

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

Starting date of project: 1st of August 2017

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 dd/mm/yyyy
2	2.3	GSOP demonstration	SINTEF		NTNU	Report	PU	30/06/2020	01/08/2020

***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

Although the proposed is to demonstrate the concept of Gas Switching Oxygen production (GSOP), the plan changed due to serious thermodynamic limitations associated with GSOP. It was decided in the consortium to change this deliverable to the demonstration of Gas Switching Partial Oxidation (GSPOX) which has shown good performance in a micro-scale for combined syngas and H_2 production with low carbon deposition [1, 2]. The GSPOX involves three steps as follows: step 1 (fuel step)- dry methane is fed to reduce the oxygen carrier and produce syngas (H_2 and CO) through methane partial oxidation with the lattice oxygen on the oxygen carrier; step 2- H_2O/CO_2 is fed to partially oxidize the oxygen carrier to produce H_2/CO; and step 3 (air step)- where the oxygen carrier is fully oxidized by air with associated heat generation (*Figure 1*).

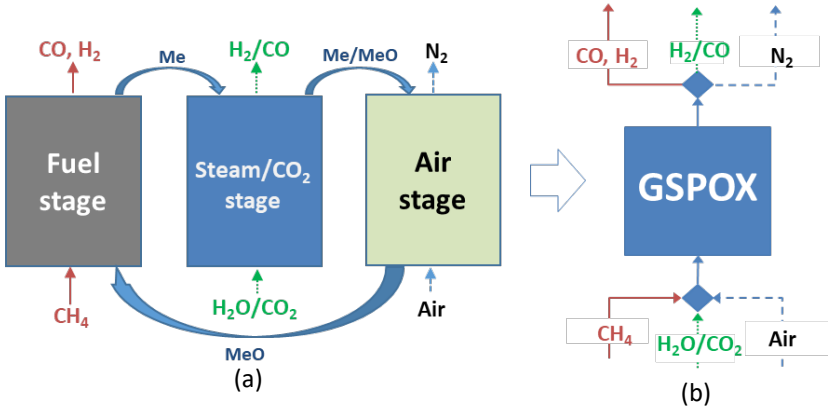

Figure 1: Three-stage chemical looping process for combined syngas production with integrated CO_2/steam utilization to produce H_2/CO. (a): Conventional chemical looping arrangement. (b): The simplified Gas Switching Technology under investigation.

A La-Fe-based perovskite ($La_{0.85}Sr_{0.15}Fe_{0.95}Al_{0.05}O_3$), that was developed, characterized and tested at a gram-scale in WP1, was upscaled to the kg-scale using spray drying in this study and tested under real gas GSPOX conditions in a dense fluidized bed [1, 2]. A high focus was placed on demonstrating the tunability of the syngas composition produced at the fuel stage to highlight the benefits of such process in delivering custom designed syngas to different downstream GTL processes. Finally, a simultaneous redox reaction mechanism for co-conversion CH_4 and CO_2 to syngas on this oxygen carrier (different from the conventional catalytic dry reforming) was experimentally demonstrated.

2 Results

Over 70% CH_4 conversion to syngas (at the fuel stage) and about 30% H_2O conversion to H_2 (at the steam stage) was achieved at 950˚C and atmospheric conditions. Despite the high reactivity and stability of this oxygen carrier, substantial carbon deposition was observed at high CH_4 concentration with a resultant increase in the syngas (H_2/CO) ratio (*Figure 2*a). The deposited carbon was completely gasified in the steam stage making carbon deposition not an issue if syngas production is targeted. However, carbon deposition can be problem if pure H_2 production is targeted in the steam stage due to the contamination by carbon gasification imposing additional purification measures. The extent of

carbon deposition was reduced by co-feeding an oxidizing gas (H_2O or CO_2) with CH_4 in the fuel stage. The addition of steam could tune up the H_2/CO ratio up to a value of 4 without carbon deposition at H_2O/CH_4 ratio of 1, 950 °C and 1 bar; making the syngas from Gas Switching Partial Oxidation (GSPOX) suitable for any downstream process, e.g. gas-to-liquid (GTL) processes. The process was also demonstrated at higher pressures with over 70 % fuel conversion achieved at 5 bar and 950 °C. Such a co-feeding option enables simultaneous oxidation and reduction of the oxygen carrier that results in steady syngas production similar to catalytic reforming (*Figure 2*b). There was no loss in activity of the oxygen carrier after the 12 h demonstration as similar trends of gas composition and temperature profile was recorded in the subsequent re-oxidation steps as observed when the fuel duration was less.

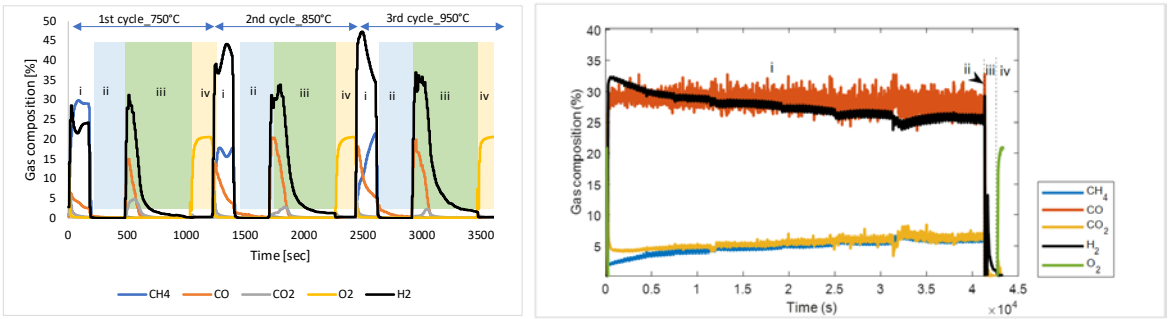

Figure 2: (a) Three cycles showing the transient gas composition under Gas Switching Partial Oxidation (GSPOX) at CH_4 molar fraction of 50 % diluted in N_2, 1 bar, and temperature from 750 to 950 °C. i: fuel stage; ii. N_2 purge; iii: steam stage; iv: Air stage. (b) Gas composition for an experiment with co-feeding of CH4 and CO_2 for over 12 hours at 800 °C.

3 Conclusion

A lanthanum-based oxygen carrier was developed and tested under the Gas Switching Partial Oxidation conditions (GSPOX) for combined syngas and H_2 production between 750 - 950 °C and pressures up to 5 bar. The results show that the oxygen carrier exhibits high selectivity to syngas production at the fuel stage with the process performance observed to improve with increasing temperature although carbon deposition could not be avoided. Co-feeding CO_2 with CH_4 at the fuel stage could reduce carbon deposition significantly and improve the purity of the H_2 produced at the subsequent steam stage. Interestingly, the demonstration of CO_2 utilization at the fuel stage showed a stable syngas production over 12 h and maintained the H_2/CO ratio at almost unity, suggesting that the oxygen carrier was exposed to simultaneous partial oxidation of CH_4 with the lattice oxygen which is restored instantly by the incoming CO_2.

References

1. Donat, F., Y. Xu, and C.R. Müller, *Combined Partial Oxidation of Methane to Synthesis Gas and Production of Hydrogen or Carbon Monoxide in a Fluidized Bed using Lattice Oxygen.* Energy Technology, 2019.
2. Donat, F. and C.R. Müller, *CO2-free conversion of CH4 to syngas using chemical looping.* Applied Catalysis B: Environmental, 2020: p. 119328.