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Techno-economic assessment of an integrated high pressure chemical-looping process with packed-bed reactors in large scale hydrogen and methanol production

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ABSTRACT

A full-scale techno-economic analysis of a novel chemical looping based process using dynamically operated packed bed reactors has been carried out for the large-scale production of hydrogen (up to 30,000 Nm³/h) and methanol (up to 10,000 tons per day) with inherently integrated CO₂ capture. The complete process is carried out in three main reactors, in which the reactions occurring are the dry and steam reforming of natural gas with H₂O and CO₂, the oxidation of the oxygen carrier (OC) with air and the reduction with a low-grade fuel such as plant off-gases. The thermal balance of the process is achieved by combining the endothermic reforming reaction with the exothermic chemical looping combustion. The chemical looping based process is fully integrated with the separation and synthesis units as well as the power and heat utilities of the two large scale production plants. The two plants are compared with state-of-the-art technologies, including the benchmarks for hydrogen and methanol production from natural gas through steam reforming and auto-thermal reforming. Compared to a conventional H₂ production plant (without CO₂ capture), the reforming efficiency is 3% higher, while the required primary energy consumption to separate CO₂ is 0.47 MJ_{LHV}/kg_{CO2} which is significantly lower than that of an amine-based plant (> 1.35 MJ_{LHV}/kg_{CO2}) and the cost of hydrogen production with the proposed process is 2.19 \$/kg with a CO₂ avoidance cost of 58.7 \$/ton_{CO2} (compared to > 70.6 \$/ton_{CO2} for solvent based plant). In case of methanol production, the carbon conversion is comparable with the best available processes even though CO₂ purification and separation (98% capture with > 96% purity) units are included due to the improved energy recovery. By using chemical looping the cost of methanol production decreases overall by 17% compared to the benchmark plant due to the lower investment cost and higher electricity generation resulting overall in a negative CO₂ avoidance cost (-303 \$/ton_{CO2}).

1. Introduction

Hydrogen (H₂) and gas-to-liquid (GTL) products such as methanol (MeOH), ammonia (NH₃) and Fischer-Tropsch fuels are among the most important chemical products in the market, and their global demand is satisfied for more than 60% by natural gas (NG) and oil/naphtha reforming (Muradov and Veziroğlu, 2005). However, the conventional reforming technology is responsible for a large part of the CO₂ emissions from chemical industries (IEA, 2015) and is accompanied by high costs. Natural gas reforming can be performed in a so-called fired tubular reforming (FTR) reactor where the natural gas reacts with H₂O to form syngas inside tubes filled with catalyst and where the tubes are immersed in a furnace using part of the fuel to supply the heat for the

endothermic reaction; a second option is the auto-thermal reforming (ATR) where an oxidant (air or pure oxygen) is fed with natural gas (NG) and H₂O to form syngas in an adiabatic reactor (Appl, 2006; Cheng and Kung, 1994; Fiedler et al., 2000; Haussinger et al., 2012). In order to reduce the greenhouse gas emissions resulting from this process, different options have been proposed in recent years to capture CO₂ from reforming and water gas shift (WGS) processes (Collodi et al., 2017), mostly based on solvent absorption and membranes, which are both hampered by high capital and/or operating costs (Abanades et al., 2015).

Chemical looping technology is an efficient alternative to separate CO₂ during the fuel conversion step. Chemical looping combustion (CLC) is based on a metal oxide, also called oxygen carrier (OC) which

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Nomenclature

AR	Air reactor	HT-IT-LT	High-Intermediate-Low Temperature
AGR	Acid Gas Removal	HTS/LTS	High temperature/Low temperature shift
ASU	Air Separation Unit	IGCC	Integrated Gasification Combined Cycle
ATR	Auto-thermal reforming	LHV	Lower heating Value
CCA	carbon capture avoidance, \$/ton _{CO2}	M	Stoichiometric Number, $M = \frac{[H_2] - [CO_2]}{[CO] + [CO_2]}$
CCF	Capital Charge Factor	MeOH	Methanol
CCR	Carbon capture rate	MDEA	Methyl diethanolamine
CCUS	Carbon capture, utilisation and storage	MEA	Monoethanolamine
CL_PB	Chemical Looping with Packed Bed	MTPD	metric tons per day (1×10^6 tons/day)
CLC	Chemical looping combustion	MW	Molecular Weight, kg/kmol
CLR	Chemical looping reforming	NG	Natural gas
COH	Cost of hydrogen, \$/kg _{H2} (unless specified)	OC	Oxygen carrier
COM	Cost of methanol, \$/ton _{MeOH}	PSA	Pressure swing adsorption
C _{O&M}	Operating and maintenance costs, M\$	SPECCA	Specific Primary Energy Consumption for CO ₂ avoided, MJ _{LHV} /kg _{CO2}
CPU	CO ₂ processing unit	TPC	Total plant cost, M\$
FTR	Fired tubular reforming	TOC	Total overnight cost, M\$
GTL	Gas to Liquid	TASC	Total as spent cost, M\$
HP-IP-LP	High-Intermediate-Low Pressure	WGS	Water gas shift
HRF	Hydrogen recovery factor, -		

is alternately reduced in presence of a fuel stream and oxidized while reacting with air (Adanez et al., 2012). Most of the research in chemical looping has been focused on chemical looping conversion of solid fuels (Adanez et al., 2018) using fluidized bed reactor configuration (Mattisson et al., 2018; Song and Shen, 2018). Among different metal oxides such as Cu-, Fe-, Mn- based oxides, NiO is the most studied oxygen carrier for CLC, predominantly supported on Al₂O₃, TiO₂ or ZrO₂ (Nandy et al., 2016). Similar concepts can be employed in order to convert fuels into syngas through partial oxidation called chemical looping reforming (CLR) in which the OC also acts as catalyst for the reforming and the shift reactions (Luo et al., 2018). The latter process has been proposed in de Diego et al. (2009) and Ortiz et al. (2010) using Ni-based oxygen carriers, because Ni can also act as catalyst for the methane reforming reactions. Due to differences in catalytic activity and oxygen transfer capacity, different oxygen carrier materials have been considered for the CLR process (Tang et al., 2015). Tso et al. (2018) have calculated that a GTL process for methanol production integrated with chemical looping can reduce the break-even oil prices for natural gas-to-liquids processes by as much as 40%, while satisfying production demands and obeying environmental constraints.

Another possible integration of reforming and chemical looping has been proposed by Ryden and Lyngfelt (2006) and in Stenberg et al. (2018), where the chemical looping reactors act as combustion chambers to provide the heat of reaction to the reforming tubes which are immersed into the fuel reactor where PSA-offgas is converted into CO₂/H₂O. Both concept have been compared from a techno-economic point of view in Spallina et al. (2017b) showing some improvements in terms of efficiency (8–10% higher) and costs of CO₂ avoidance (CCA) ranging from 20–85 €/ton_{CO2}. Similar results has been obtained by Nazir et al. (2018) who assessed the cost of pre-combustion configuration using CLR as a syngas generation technology and by Symonds et al. (2019) for the production of heat for the steam-assisted gravity drainage (SAGD) process in oil sand field and syngas for GTL process.

A different reactor concept has been proposed and recently experimentally demonstrated in a 500 W_{LHV} interconnected circulating fluidized bed (i-FBR) chemical looping membrane reformer (Medrano et al., 2014, 2018): compared to standard CLR process, in this configuration, in-situ pure H₂ separation through metallic Pd-based membranes occurs and the fuel species are converted to CO₂ and H₂O so that no other conversion and separation processes are required in the plant resulting in a higher reforming efficiency compared to an existing H₂ production plant (91% vs 74%) and a negative CCA (-25 €/ton_{CO2}) as

reported in Spallina et al. (2016). Similar to that, a membrane assisted chemical looping switching reforming technology have been proposed by (Wassie et al., 2018b) in which the membrane reactor are dynamically operated to circumvent the high pressure stability associated in i-FBR. In this case the overall performance is slightly better than benchmark technologies based on amine technologies (CCA lower than 12%) (Wassie et al., 2018a).

Another concept for H₂ production using chemical looping has been demonstrated at the Ohio State University using Fe-based OC combined with an intermediate oxidation stage which is carried out with H₂O to form pure H₂. They found a net efficiency higher than 6% - 10% compared to conventional FTR and ATR baseline configuration (Kathe et al., 2016; Nadgouda et al., 2019).

Khan and Shamim (2016) have calculated a cost of H₂ production which is significantly low when compared to the case of steam methane reforming with CO₂ capture (about 30% lower and comparable with H₂ production from steam methane reforming technology (1.404 \$/kg vs 1.68\$/kg).

Other alternative processes have considered the integration of high temperature solar energy to sustain the reforming reaction (Fosheim et al., 2018; Krenzke et al., 2017) and the integration of sorption-enhanced reforming and chemical looping to simultaneously carry out H₂ production and CO₂ separation in a single process resulting respectively in a cost of H₂ production 8% lower than a conventional FTR configuration (Fernandez et al., 2017; Martini et al., 2016; Riva et al., 2018).

A different chemical looping concept for both combustion and reforming has been proposed by Spallina et al. (2017a) using packed bed reactor technology (CL_{PB}). Starting from a previous research project on chemical looping combustion integrated with IGCC for power production (Hamers et al., 2015; Spallina et al., 2013, 2015b) the proof of concept and model validation has been carried out in a 500 g lab-scale reactor using Ni/CaAl₂O₄ as oxygen carrier previously tested and characterised (Medrano et al., 2015).

In this work, the packed-bed reactor chemical looping technology has been integrated and assessed for H₂ and MeOH production. Despite only two works have been published so far on chemical looping for methanol production, the synergies of the two processes are very promising and therefore this process has been studied and presented with details in this work. The chemical looping process is carried out with packed process at high pressure and fully integrated with the other parts of the plant. The reactor performances are calculated using the existing and validated 1D reactor model. For the selected

configurations, an economic assessment is carried out and a sensitivity analysis on natural gas cost, reactor cost, and oxygen carrier durability is presented to provide a complete overview of their potential profitability in comparison with current technologies with and without CO₂ capture.

In the first part of the paper, the assumptions and methodologies are discussed including the description of the benchmark technologies considered for the comparison; after that the full techno-economic analyses respectively for the hydrogen and methanol production are carried out including the sensitivity analysis and finally the major conclusions are reported.

2. Assumptions and Methodologies

2.1. Benchmark hydrogen production

The state-of-the-art for H₂ production is based on fired tubular reforming plant (FTR) and has been reported in (IEAGHG, 2017) and described extensively in previous works (DOE/NETL, 2010; Martínez et al., 2013; Molburg and Doctor, 2003). In this plant, natural gas (NG) is initially treated to convert sulphur compounds to H₂S and saturate any olefins in a catalytic hydrogenation and later adsorb H₂S over a bed of ZnO. The NG is then mixed with H₂O and pre-reformed to convert the higher hydrocarbons before the primary reforming. The pre-reformed natural gas is pre-heated and introduced into an externally heated fired tubular reformer where the gas mixture is converted into synthesis gas (syngas) at 890 °C in tubes filled with catalyst (generally Ni-based). The reformed syngas is cooled down and fed into the high temperature shift (HTS) reactor to convert the CO to H₂ thus producing a syngas with a residual CO of around 2.5–3%. Three different benchmark plants have been considered:

- 1) **Base case (H₂-BC).** After cooling the shifted syngas to ambient temperature, a PSA (Pressure Swing Adsorption) unit is used to separate pure H₂ (> 99.9%) and the PSA-offgas is combusted in the reformer burner to supply the heat for the endothermic reactions. The heat for the steam reforming reaction is supplied by burning the PSA-offgas and part of the NG with air in the furnace. Waste heat recovery downstream of the furnace is carried out in convective banks in which the reforming reactants are pre-heated.
- 2) **Mild CO₂capture (H₂-MCC).** A second low temperature water gas shift (LTS) reactor is considered to achieve a final CO content below 0.2% with an overall CO conversion in WGS section higher than 98%. The H₂-CO₂ rich mixture is cooled down and the CO₂ is separated from the H₂ by means of methyl-di-ethanol amine (MDEA) absorption. The captured CO₂ is then released and the solvent regenerated in a desorber column. A PSA is used to separate H₂ at high purity, as in the H₂-BC configuration. NG and air are feed to the furnace to supply the heat for the reforming reaction and the flue gases are vented to the atmosphere.
- 3) **High CO₂capture (H₂-HCC).** This configuration presents the same conversion and separation units as the base case (H₂-BC) but with CO₂ capture from the flue gas using mono-ethanol-amine (MEA) solvent post-combustion capture technology. In this configuration, the CO₂ separation rate is 90% (Collodi et al., 2017) and the flue gas is first cooled down to ambient temperature, then compressed to 1.06 bar and sent to the absorber. The CO₂ is later separated by the solvent by using LP steam to supply the heat at the reboiler.

The H₂-BC plant leads to large CO₂ emissions (above 840 gCO₂/NmH₂³) to the atmosphere, associated with the combustion of the PSA-offgas and part of the fuel. The H₂-MCC leads to a CO₂ emission reduction of slightly below 65%, while the H₂-HCC emissions are reduced by 90% compared to H₂-BC.

2.2. Benchmark methanol production

Large scale methanol (MeOH) production from natural gas is typically carried out in an oxygen-blown auto-thermal reforming (Aasberg-Petersen et al., 2003). In this study, a large scale methanol plant with a capacity of 10,000 MTPD (metric tons per day) (Kim Aasberg-Petersen et al., 2013) has been taken as benchmark technology representative of a methanol-to-olefins production unit. A natural gas to methanol plant combines three different conversion units: oxygen production, syngas generation and methanol synthesis/purification. The O₂ required for the ATR reactions is produced in a cryogenic Air Separation Unit (ASU). The ASU modelling is beyond the scope of this work and therefore data from literature are taken from different references (Beysel, 2009; Crotti, 2010; Jones et al., 2011). The ASU is a conventional, cryogenic, pumped liquid oxygen unit that provides oxygen for the reforming process. The ASU is designed to produce 95%mol purity for use in the reformer. The air compressor is powered by an electric motor. The reference for ASU is based on a two thermally integrated separation columns layout. The O₂ (with purity of 95%) is pumped to the ATR pressure and heated up (where the liquid O₂ is evaporated) supplying part of the refrigeration duty to the cooling of the inlet air to the separation column(s). Syngas generation has been studied in two different layouts:

- 1) **Single stage auto-thermal reforming (1s-ATR).** In this configuration, NG is combined with oxygen and steam, pre-heated to 680 °C and fed to an auto-thermal reactor as suggested in (DOE/NETL, 2014a). The steam-to-carbon ratio (S/C) is equal to 0.3 while oxygen-to-carbon ratio (O/C) equal to 1.07. The reforming is accomplished through contacting the reaction mixture with a nickel catalyst supported on alumina. A purified oxygen feed was chosen to minimize the amount of inert gases introduced into the methanol synthesis loop. The ATR operates at (30 bar and 1100 °C). It must be noted that in this case CH₄ is converted in a single unit since pre-reforming would not be feasible unless higher S/C ratios would be used. Pure O₂ is fed to achieve an overall CH₄ conversion > 95% and a gas mixture of H₂, CO and CO₂ (represented by the stoichiometric number M (Fiedler et al., 2000) as in equation 1) which maximizes the MeOH yield;

$$M = \frac{[H_2] - [CO_2]}{[CO] + [CO_2]} \div 1.8 - 2 \quad (1)$$

- 1) **Two-step reforming (2s-ATR).** The two-step reforming process features a combination of fired tubular reforming (also called primary reformer, operated at mild temperature, $\approx$ 750 °C) followed by an oxygen-fired adiabatic reforming to complete the CH₄ conversion as proposed by Haldor-Topsøe (Kim Aasberg-Petersen et al., 2013). In this case, IP steam from the heat recovery and power generation units is mixed with NG (steam-to-carbon ratio of 1.8) and preheated to 500 °C before being sent to an adiabatic pre-reformer; the pre-reformed syngas is pre-heated to 620 °C and sent to a primary reforming unit operated at equilibrium conditions at 32 bar and 750 °C. Almost 65% of CH₄ is converted in the primary reformer, while complete conversion occurs in a secondary auto-thermal reforming unit, to which O₂ is fed.

The reformed syngas is cooled to recover heat at a useful temperature to produce HP/IP steam respectively at 100 bar and 40 bar. As the syngas is cooled, process condensate, feed water, and raw water are being heated. The syngas is finally sent to the multi-stage syngas compressor. Part of the electricity required for the syngas compression to methanol synthesis unit is compensated by power generation with a steam turbine.

The methanol synthesis has been designed according to the baseline analysis proposed in the DOE-NETL report (DOE/NETL, 2014a). The process consists of catalytic packed bed reactor operated with vapour

phase methanol. The reactor is steam cooled to facilitate near isothermal operation at 55 bar and 250 °C. Because the methanol synthesis reaction is equilibrium limited (DOE/NETL, 2014a; Fiedler et al., 2000), the methanol reactor effluent is cooled to condense out the product crude methanol that is removed with a phase separator. In the 1s-ATR configuration, 95% of the gases are recirculated and fed back to the methanol reactor along with fresh syngas while the 5% left is sent to a small furnace to generate some heat for the pre-heating of the reactants. In the 2s-ATR, approximately 16% of the unconverted syngas is sent to the furnace of the primary reforming and therefore not recirculated to the MeOH synthesis reactor. The liquid fractions (mainly MeOH and H₂O) enter the first distillation column at 2 bar. MeOH with 85% purity enters the second distillation column for additional separation, to reach > 99% purity.

2.3. Assumptions and key performance indicators

The assumptions for the design of the plant and the thermodynamic assessment have been chosen from available literature and validated accordingly (DOE/NETL, 2010, 2014a; EBTF, 2011; IEAGHG, 2017).

- 1) Reforming units: the reforming reactions are considered to be at their chemical equilibrium. The reforming pressure is taken equal to 30 bar for all cases. The reactors used for chemical looping have been designed according to two previous works on CLC/CLR with packed bed reactors (Spallina et al., 2017a, 2015a).
- 2) Acid Gas Removal (AGR): the simulation of acid gas removal is based on amine-based solvent. The reboiler heat duty, the electric consumptions of the pump for solvent circulation, and the specific cost of the complete equipment have been taken from literature (DOE/NETL, 2010; EBTF, 2011; Spallina et al., 2016).
- 3) H₂ purification is carried out in a Pressure Swing Adsorption unit (PSA) for which hydrogen recovery of 89% is assumed (Spallina et al., 2016).
- 4) Air Separation Unit (ASU): the ASU has not been modelled, but the mass and energy balances are derived from literature data (Beysel, 2009; Crotti, 2010; Jones et al., 2011; Linde Engineering, n.d.; Smith and Klosek, 2001). The specific energy consumption for the production of oxygen with 95% purity ranges from 200 – 300 kWh_{el}/ton_{O₂}. In this work the specific consumption has been set equal to 250 kWh/ton_{O₂}, corresponding to 0.9 MJ/kg_{O₂}. The sizing of the ASU is based on the maximum plant capacity available (around 7000 t_{O₂}/d per unit, approximately 81 kg/s as for the 1s-ATR).
- 5) Turbomachines: the blowers, pumps, compressor, expanders and steam turbine are calculated assuming isentropic and electro-mechanical efficiencies from which the thermodynamic conditions of the outlet streams and the energy balance is derived (Table 1).
- 6) Heat exchangers are modelled in order to achieve a minimum pinch temperature difference which is assumed equal to 5 °C (liquid-liquid), 10 °C (gas-liquid) and 25 °C (gas-gas).

The comparison has been carried out, using some key technology parameters listed below (eq. 2–12):

Equivalent natural gas flow rate	$\dot{m}_{NG,eq} = \dot{m}_{NG} - \frac{\dot{W}_{el}}{\eta_{el,ref} \cdot LHV_{NG}} - \frac{\dot{Q}_{th}}{\eta_{th,ref} \cdot LHV_{NG}}$	(2)
Steam-to-export	Where $\eta_{el} = 0.583$; $\eta_{th} = 0.9$ $\dot{Q}_{th} = \dot{m}_{steam} \cdot (h_s @ 6bar - h_{liq,sat} @ 6bar)$	(3)
Process Efficiency for H ₂	$\eta_{H_2} = \frac{\dot{m}_{H_2} \cdot LHV_{H_2}}{\dot{m}_{NG} \cdot LHV_{NG}}$	(4)
	$\eta_{H_2,eq} = \frac{\dot{m}_{H_2} \cdot LHV_{H_2}}{\dot{m}_{NG,eq} \cdot LHV_{NG}}$	
Process Efficiency for MeOH	$\eta_{MeOH} = \frac{\dot{m}_{MeOH} \cdot LHV_{MeOH}}{\dot{m}_{NG} \cdot LHV_{NG}}$	(5)
	$\eta_{MeOH,eq} = \frac{\dot{m}_{MeOH} \cdot LHV_{MeOH}}{\dot{m}_{NG,eq} \cdot LHV_{NG}}$	

$$CO_2 \text{ specific emissions (E}_{CO_2}) = \frac{\dot{m}_{CO_2}}{\dot{m}_{prod,i}} \quad (6)$$

$$\text{Specific Energy Consumption for } CO_2 \text{ Avoidance} = \left(\frac{1}{\eta_{H_2,eq}} - \frac{1}{\eta_{H_2,ref,eq}} \right) \cdot LHV_{NG} \left[\frac{MJ_{NG,LHV}}{kg_{CO_2}} \right] \quad (7)$$

$$\text{Energy consumption} \quad HR_{H_2} = \frac{\dot{m}_{NG} \cdot LHV_{NG} - \dot{W}_{el} - \dot{Q}_{th}}{\dot{N}_{H_2,vol}} \cdot \frac{1}{4.186} \left[\frac{Gcal_{NG,LHV}}{kNm_{H_2}^3} \right] \quad (8)$$

$$HR_{MeOH} = \frac{\dot{m}_{NG} \cdot LHV_{NG} - \dot{W}_{el} - \dot{Q}_{th}}{\dot{m}_{MeOH}} \left[\frac{Gcal_{NG,LHV}}{ton_{MeOH}} \right]$$

$$\text{Carbon conversion} \quad \eta_C = \frac{\dot{N}_{MeOH}}{\sum \dot{N}_{i,NG} \cdot n_{c,i}} \quad (9)$$

$$\text{Cost of product: COH, COM} \quad COP = \frac{(TASC \times CCF + CO + M_{fix} + CO + M_{var})_y}{(\dot{m}_i)_y} \quad (10)$$

$$\text{O\&M variable} \quad CO \& M, var = C_{fuel} + C_{el} + C_{steam} + C_{solid_replac} \quad (11)$$

$$\text{Cost of } CO_2 \text{ avoidance, CCA} \quad CCA = \left(\frac{COP_i - COP_{ref}}{E_{CO_2,ref} - E_{CO_2,i}} \right) \quad (12)$$

2.4. Economic model

The economic analysis is based on the model proposed by DOE (DOE/NETL, 2010, 2011, 2014a) and reported in Table 2.

The cost of the H₂ production plant has been derived from (DOE/NETL, 2010; EBTF, 2011; IEAGHG, 2017; Riva et al., 2018; Spallina et al., 2016). Exponential scaling law has been used to calculate the equipment cost as function of scaling parameters as commonly suggested in the reported in chemical engineering handbook (Sinnott and Towler, 2013; Smith, 1994). The costs are updated to 2018 according to the Chemical Engineering Plant Cost Index, (CEPCI) (Table 3).

The chemical looping reactor network has been designed according to the results of the model as discussed later. Apart from the reactors required to carry out the complete process, two extra units are considered for the purging phase before and after OC oxidation and 25% more reactor volume is considered in order to have some spare units during maintenance. Each reactor includes high temperature valves for the switching operation. The cost of the reactor is based on the design and costing proposed in the FP7 ASCENT project (<http://ascentproject.eu/>) and FP7 Democlock project (<http://www.sintef.no/Projectweb/DemoClock/>) and published in Mancuso et al. (2017).

The operating costs are derived from the unitary cost of consumables as reported in Table 4.

The comparison is based on the required selling price of the products, and is calculated using the capital charge rate factor (CCF), which defines a characteristic unit cost of the plant per year. This is calculated taking all the expenditures that occur in different periods into account, so that the required return on equity (ROE) equals the internal rate of return (IRR) for plant life time of operation, based on the assumed financial structure and escalations as reported in Table 5. The resulting CCF are 0.159 and 0.158 respectively for H₂ and MeOH production which is different from the DOE studies due to the different assumptions in the financial model (0.184 for H₂ in DOE/NETL (2010) and 0.17 for MeOH in DOE/NETL (2014a).

Table 1
Main parameters used for the modelling of turbomachines.

components	η_{is}	η_{m-e}	Cost reference
Blowers	0.75	0.95	(Manzolini et al., 2006)
Compressors	0.85	0.95	(Baasel, 1989; Dutch Association of Cost Engineers, 2014)
Pumps	0.85	0.95	(Baasel, 1989; Dutch Association of Cost Engineers, 2014)
Expander	0.85	0.99	(Baasel, 1989; Dutch Association of Cost Engineers, 2014)
HP Steam Turbine	0.85	0.99	(Manzolini et al., 2013)
LP Steam Turbine	0.75	0.99	(Manzolini et al., 2013)

Table 2
Methodology for the calculation of the TASC.

Equipment cost [EC] of i-component		M\$
Material cost [MC] of i-component		M\$
Labor cost [LC] of i-component		M\$
Bare Erected Cost [BEC _i] of i-component		M\$
BEC = ΣBEC_i		M\$
Engineering procurement and construction [EPC]	10% of BEC	M\$
Contingency [CON]	20% (BEC + EPC)	
Total Plant Cost [TPC]	BEC + EPC + CON	M\$
Owner cost & other financial cost [O&OFC]	20% of TPC	
Total Overnight Cost [TOC]	TPC + O&OFC	
Total as spent cost [TASC]	TOC + 18%	M\$

3. Chemical Looping packed bed process

3.1. Concept

Chemical looping with packed bed reactors (CL_{PB}) for natural gas reforming consists of a combination of three conversion units in which gas-solid and catalytic reactions occur (Fig. 1). Compared to the interconnected fluidised bed, this system is dynamically operated. In packed bed gas-solid reactor, the reaction front moves towards the end of the reactor faster and therefore it is possible to accumulate heat inside the reactor (in presence of an exothermic reaction as in the case of oxidation) and then remove the heat by producing high temperature gas for power generation or an endothermic reaction as in the case of steam reforming (Spallina et al., 2019).

In the presence of an OC (e.g. Ni-based), the reactor operated in *oxidation* converts the MeO_{α-1} into MeO_α by reaction with air while releasing N₂. The reactor operated in *reduction*, converts the OC to MeO_{α-1} using low grade fuel available in the plant from downstream processes producing CO₂ and H₂O. Finally, a third reactor operated in *reforming*, where the OC is in its reduced form, is fed with natural gas together with recirculated CO₂/H₂O from the reduction phase to convert CH₄ into reformed syngas. Some additional dilution is required to increase the CH₄ conversion and adjust the CO/H₂ ratio required for the downstream process, however part of the reforming reactants are taken from the reduction outlet. In the case where only H₂O/CO₂ is used, the reformat syngas is richer in CO. This concept has been presented for the first time by the authors in Spallina et al. (2017a) and was also applied to other similar process such as chemical looping switching reforming as proposed in Francisco Morgado et al. (2017) and Zaabout et al. (2019).

Table 3
List of reference cost and scale factor used for the calculation of TPC.

Equipment	Scaling parameter	unit	capacity _{ref}	(TPC) _{ref} M\$	f	year	Reference
Air Separation Unit	oxygen flowrate	kg/s	86	636.39	0.89	2007	DOE/NETL (2014a)
Auto-thermal Reformer including HE and compressors	syngas flowrate	kmol/h	13.73	434.60	0.82	2007	DOE/NETL (2014a)
MeOH synthesis and separation	MeOH flow rate	kg/s	115.42	397.34	0.82	2007	DOE/NETL (2014a)
Steam Turbine, large	Net Power	MW	105	85.03	0.72	2007	DOE/NETL (2014a)
Steam Turbine, small	Net Power	MW	1.65	1.71	0.67	2017	DOE/NETL (2010)
Cooling plant unit	Heat rejected	MW _{th}	470	38.17	0.67	2017	
BOP	MeOH flow rate	kg/s	115.42	89.97	0.67	2007	DOE/NETL (2014a)
electric, control and piping	Auxiliary load	MW	194	153.43	0.8	2007	DOE/NETL, 2014a
Fired Tubular Reforming (including pre-reforming)	Heat of reaction	MW _{th}	245	76.35	0.67	2007	DOE/NETL, 2010
ZnO sulphur polisher	NG inlet flow rate	kg/s	23.60	0.32	0.82	2007	DOE/NETL (2010)
Air blower	Air flow rate	kg/s	207.51	1.14	0.72	2007	DOE/NETL, 2010
WGS reactors	Inlet syngas flowrate	kg/s	117.98	17.05	0.82	2007	DOE/NETL, 2010
MDEA, CO ₂ separation	CO ₂ flow rate	kg/s	47.81	147.82	0.8	2007	DOE/NETL (2010)
MEA, CO ₂ separation	CO ₂ flow rate	kg/s	16.44	104.99	0.8	2007	DOE/NETL (2010)
CO ₂ compressor	Power consumptions	MW	23.02	21.77	0.72	2007	DOE/NETL, 2010
PSA	Inlet syngas flowrate	m ³ /s	4.63	50.22	1	2007	DOE/NETL, 2010
Gas turbine	Inlet air flow	kg/s	209	40.85	0.85	2007	DOE/NETL (2014a)
syngas coolers	UA	MW/K	1.31	2.67	0.22	2017	Riva et al. (2018)
Chemical looping reactors (including valves, piping, etc.)	Reactor volume	m ³	261.3	11.57	1	2017	Mancuso et al. (2017)

Table 4
Assumptions for the calculation of the O&M costs (DOE/NETL, 2010, 2014a).

O&M -Fixed		H ₂ plant	MeOH plant
Labor costs	M\$	2.0	4.5
Maintenance cost	% TASC	0.7	0.7
Insurance	% TASC	1.5	1.6
Catalyst and sorbent replacement			
Oxygen carrier cost	\$/kg	20	20
Reforming catalyst cost	\$/kg	50	50
Water gas shift catalyst cost	\$/kg	60	
Desulphurization catalyst cost	\$/kg	15	
Methanol synthesis catalyst	k\$/t		40
Lifetime catalyst	years	5	
Lifetime oxygen carriers	years	2	
Consumables & Miscellaneous			
Natural gas cost	\$/GJ _{LHV}	6.5	
Steam cost ^a	\$/ton _{steam}	0.13	
Electricity cost (generated)	(\$/MWh)	55	
Electricity cost (purchased)	(\$/MWh)	105	

a: based on the equivalent electricity to be produced

Table 5
Assumption for the financial model (DOE/NETL, 2010, 2014a; Spallina et al., 2016).

	H ₂ plant	MeOH plant
inflation	0.03	
taxation rate	0.35	
Depreciation (Year)	20	30
debt interest rate	0.05	
revenue interest rate	0.15	
Revenue fraction	0.4	
Debt fraction	0.6	
Construction Payment Years	3	5
→payment 1st year	40%	10%
→payment 2nd year	30%	30%
→payment 3rd year	30%	25%
→payment 4th year	-	20%
→payment 5th year	-	15%
Life time	20	30
Equivalent hrs	7500	
Construction Years	3	5

- with respect to conventional fired tubular reforming (FTR) plants, the CL_{PB} process does not require an external furnace and high temperature heat transfer surface, because the process is auto-thermal;

Fig. 1. Schematic of the chemical looping process with PBRs, CL_PB.

- with respect to an ATR process, the oxygen is supplied to the reaction through the OC, therefore a cryogenic air separation unit is not required;
- with respect to the dual-fluidized bed chemical looping reforming, the CL_PB with PBRs can be easily operated at higher pressure. Moreover, intrinsic CO_2 separation is achieved in the CL_PB, which delivers a high-pressure CO_2 stream without the need of a dedicated process based on amines or other non-commercial technologies as proposed in another work (Ortiz et al., 2011);
- with respect to the integrated reformer with CLC (Pans et al., 2013; Ryden and Lyngfelt, 2006) and all the other mentioned alternative technologies, the steam consumption can be reduced owing to the $\text{CO}_2/\text{H}_2\text{O}$ recirculation.

3.2. Model Description

The model used for the present investigation is based on a 1D adiabatic axially dispersed packed bed reactor model discussed in several previous works from the authors and already validated in two

lab scale facilities at Eindhoven University of Technology (Gallucci et al., 2015; Spallina et al., 2017a). The kinetic model is based on the use of Ni based OC (17–18.5% wt.) supported on CaAl_2O_4 which has been tested and characterised in Medrano et al. (2015). The main model assumptions are: i) no radial profiles; ii) pseudo-homogeneous model; iii) heat losses are negligible due to the large reactor diameter. The governing equations for the reactor model are reported in (Spallina et al., 2017a) including the results for the reactor heat management and operation. The simulation and results for the heat management of the chemical looping reactors for MeOH production have been updated to the new process configuration (in terms of plant size, gas flowrates, composition and temperature) and therefore presented in 4.3 section while for the chemical looping reactors for H_2 production the results were reported in our previous work (Spallina et al., 2017a).

4. Analysis of Results

4.1. Hydrogen production

The first plant presented in this work is CL_PB in packed beds for H_2 production as shown in Fig. 2.

Natural gas (NG, stream #1) is pre-heated to 280°C and sulphur is removed in a ZnO bed. NG is then mixed with medium pressure H_2O from the steam cycle, pre-heated to 580°C and mixed with part of the $\text{CO}_2\text{-H}_2\text{O}$ recirculated from the reduction and finally fed to the reforming reactor (REF, stream #4). The syngas is then cooled and sent to a high-temperature WGS (at 400°C) to increase the conversion of CO to CO_2 and H_2 (#6). H_2 from syngas is then separated at high purity (#7) in a conventional pressure swing adsorption (PSA). The PSA-offgas is compressed up to 35 bar and mixed with a small amount of CH_4 for the reduction process (RED, stream #9). The resulting gas (72.9% CO_2 , 26.4% H_2O , 0.7% others) is partly fed to the reformer (50%) in order to dilute the CH_4 and increase both the CO_2/CH_4 and $\text{H}_2\text{O}/\text{CH}_4$ ratios. Finally, compressed air (#13) is sent to the oxidation reactor (OXI) to regenerate the OCs.

The overall mass balance and the main thermodynamic properties of each stream are listed in Table 6.

The energy balance and key performance indicators comparison has been carried out with the state-of-art technologies proposed for H_2 production including CO_2 capture through solvent processes. The results are shown in Table 7.

In case of H_2 production with CO_2 capture from flue gas from the

Fig. 2. Integration of chemical looping process for H_2 production.

Table 6Mass balance of the MeOH-CL_{PB} plant for H₂ production as shown in Fig. 2.

#p	p bar	T °C	N kmol/s	m kg/s	MW kg/kmol	H ₂ O	Composition (%vol.)						
							N ₂	O ₂	H ₂	CO	CO ₂	CH ₄	C ₂₊
1	70.0	15.0	0.15	2.62	18.02		0.01				0.02	0.89	0.08
2	35.0	296.6	0.12	2.09	18.02		0.01				0.02	0.89	0.08
3	30.3	580.0	0.45	8.11	17.93	0.74			0.01		0.01	0.23	0.02
4	30.3	699.6	0.67	16.13	24.12	0.58					0.24	0.15	0.01
5	30.0	960.0	0.91	16.13	17.75	0.35			0.34	0.18	0.13		
6	29.1	400.0	0.91	16.13	17.75	0.21			0.47	0.05	0.26		
7	29.0	31.0	0.38	0.76	2.02				1.00				
8	31.6	402.1	0.33	11.86	35.58		0.01		0.14	0.13	0.71	0.01	
9	35.0	391.5	0.36	12.39	34.16		0.01		0.13	0.12	0.66	0.08	0.01
10	31.6	937.0	0.43	16.03	37.05	0.26	0.01				0.73		
11	31.6	350.0	0.22	8.02	37.05	0.26	0.01				0.73		
12	110.0	30.0	0.16	6.99	43.88		0.01				0.99		
13	31.6	554.2	0.54	15.62	28.85		0.79	0.21					
14	29.6	664.5	0.46	12.48	27.41	0.06	0.94						
15	1.0	192.3	0.46	12.48	27.41	0.06	0.94						
16	92.0	474.5	0.66	11.82	18.02	1.00							
17	6.0	161.6	0.30	5.32	18.02	1.00							
18	40.0	358.1	0.33	6.02	18.02	1.00							
19	40.0	358.1	0.03	0.49	18.02	1.00							

furnace (H₂-HCC) and syngas (H₂-MCC), the same reforming efficiency of the reference reforming plant is achieved (H₂-BC). In H₂-HCC, most of the performance drops are associated with the required high consumption of LP steam (the steam from the steam turbine is insufficient) and therefore part of it needs to be imported. The net power production also decreases due to the booster required for the exhaust gas and the CO₂ compression. The resulting energy penalty for CO₂ capture is 2.56 MJ/kg_{CO2} of primary energy.

In case of partial CO₂ separation (from shifted syngas, H₂-MCC) only 63.6% of CO₂ is separated, because some NG is still required in the furnace. Despite the reforming efficiency does not changing with respect to the H₂-BC case, the efficiency penalty is limited to 73.7% (compared to 63.6% of H₂-HCC) because of the lower heat consumption for MDEA regeneration and the lower CO₂ separation rate. The combination of CCR and energy efficiency results in primary energy consumptions for CO₂ avoided of 1.35 MJ/kg_{CO2}.

The integration of a chemical looping process for CO₂ capture (H₂-CL_{PB}) shows a better reforming efficiency than other steam reforming

plants (75% vs 72%). This is due to the fact that the temperatures of the streams from reduction and oxidation at the outlet of the PBR do not necessarily need to exceed the reforming temperature as is the case in the furnace of the FTR. However, a higher electricity consumption is required to run the entire plant mostly because of the offgas compressor to the reduction reactor. The electricity generated from the gas turbine is overall negative due to the combination of a lower flow rate during expansion than compression (depleted air vs air) and a low turbine inlet temperature with respect to a conventional gas turbine in combined cycle (705 °C vs > 1300 °C). On the other hand, a larger steam-to-export is obtained due to the high amount of low-temperature heat available in the plant. The H₂-CL_{PB} plant achieves 98% of CO₂ capture rate due to the fact that all the carbon compounds from the PSA (mostly CO/CO₂ and traces of unconverted CH₄) are converted in the reduction reactor into CO₂ and separated downstream except some possible leakage during purge. The overall equivalent reforming efficiency and heat rate results are very close to the one of H₂-BC, and this is also shown by the overall SPECCA of only 0.48 MJ/kg_{CO2}.

Table 7Energy balance and key performance parameters for the selected configurations (H₂ production).

Hydrogen Production		H ₂ -BC	H ₂ -HCC	H ₂ -MCC	H ₂ -CL _{PB}
		N/A	MEA flue gas	MDEA syngas	Chemical Looping
NG flow rate		2.62	2.62	2.62	2.62
NG thermal Input		121.94	121.94	121.94	121.94
H ₂ mass flowrate		0.73	0.73	0.73	0.764
Electricity prod/cons					
Fan/boosters		−0.37	−0.50	−0.78	−5.18
Gas turbine (comp + exp)					−2.97
CO ₂ compressors			−2.18	−1.54	−0.59
CO ₂ separation			−0.05	−0.04	
Steam Turbine		3.11	3.11	3.11	3.76
LP/HP pumps		−0.20	−0.20	−0.22	−0.23
other auxiliaries		−0.04	−0.33	−0.08	−0.11
net electric power		2.50	−0.14	0.45	−5.35
steam export (160 °C, 6 bar)		4.38	−6.70	1.17	5.32
Ref. efficiency η_{H_2}		72%	72%	72%	75%
Equivalent NG $m_{NG,eq}$		2.31	2.96	2.55	2.56
H ₂ yield		2.41	2.41	2.41	2.52
Eq. Ref. efficiency $\eta_{H_2,eq}$		81.5%	63.6%	73.8%	77.1%
Heat Rate		3.22	3.97	3.48	3.24
CO ₂ specific emissions, E _{CO2}		9.51	0.95	3.47	0.19
CO₂ avoided (respect to H₂-BC)		0%	90%	64%	98%
SPECCA (referred to η_{eq})			2.56	1.35	0.48

4.2. Cost of hydrogen production

The economic comparison is reported in Table 8. The H₂-BC cost is mostly related to the reforming section (55.4% of the total TPC), and PSA (15% of TPC). H₂-HCC has the highest cost due to the additional CO₂ absorption unit which represents more than 50% of the entire investment cost. Compared to H₂-HCC, the H₂-MCC has a lower cost of CO₂ separation since CO₂ is more concentrated in the syngas and only 64% of CO₂ is separated. WGS reactors are more expensive due to the presence of a LT stage. For the given mass and energy balances of H₂-CL_{PB} shown in Table 6, overall 6 reactors are considered of 3.5 m internal diameter and 10.5 m length of which 1 reactor is operated respectively in OX/PURGE/RED/REF/PURGE and 1 spare reactor is present in the plant to assist any maintenance issue. In case of H₂-CL_{PB}, the TPC cost is 37% higher than H₂-BC but lower than benchmark CO₂ capture based technologies, which is related to the fact that the in-situ CO₂ separation in the fuel reactor does not add additional cost to the reforming unit. The syngas flow rate, due to the higher CO₂ content (26% vs 13% after the WGS) is about 30% higher compared to H₂-HCC and H₂-BC and therefore the cost of WGS reactor and PSA is significantly higher (65% higher for the WGS and 37% higher for the PSA with respect to the H₂-BC configuration).

Looking at the variable costs, it is important to note that for the benchmark technologies, the only relevant cost is dictated by the natural gas feedstock. Additionally, in the case of H₂-CL_{PB} the cost for the OC replacement and the cost of electricity to be purchased from the network are also relevant in the final annual cost. The cost of OC replacement is mostly influenced by the selected life time (2 years) and the price since the analysis is based on a synthetic material.

Overall the cost of hydrogen (COH) for the H₂-CL_{PB} is 30% higher than the H₂-BC. In terms of cost of CO₂ avoidance, the analysis shows that the cost H₂-CL_{PB} is 40% lower than H₂-HCC and 24% lower than H₂-MCC: in the first case the lower cost of H₂ production results from the reduced CCA, while in the second case the higher CO₂ capture rate (100% vs 64%) makes the chemical-looping technology more advantageous.

Related to the uncertainties on the cost of the novel chemical looping technology, a sensitivity analysis on the COH and CCA has been carried out by varying the cost of the technology and the OC lifetime and cost. The cost of the technology has been varied from 50% lower to 300% higher with respect to the basic scenario.

The lifetime of the OC has been considered respectively from 6 months as the current state-of-the-art OC tested in an existing laboratory, up to 5 years which is comparable to the lifetime of commercial catalysts.

The cost of OC has been varied from 2 \$/kg as in the case of Fe₂O₃-based OC or natural ore such as ilmenite as assumed in DOE/NETL (2014b) and in Mancuso et al. (2017) to 80 \$/kg which is comparable to the cost of an existing high Ni content catalyst as experimentally used in Medrano et al. (2015) and Spallina et al. (2017a) or in the scenario of high cost OC.

The results of the sensitivity analysis are shown in Fig. 3 and they all demonstrated that only for the worst case scenarios such as cost of the reactor > 200%, cost of the OC > 50 \$/kg and OC lifetime < 1 year, the H₂-CL_{PB} is no longer competitive with the other technologies considered in this study. When combining the best scenarios, the cost of hydrogen production from H₂-CL_{PB} is just 15% higher than the H₂-BC and the resulting CO₂ avoidance cost drops to 27.05 \$/ton_{CO2}, which is already convenient in the case of a low carbon tax scenario.

4.3. Methanol production

In case of MeOH production, the chemical looping process is very similar to the one described for H₂ production (Fig. 4). In this case, the incondensable gases (#11) are partly recirculated to the methanol synthesis reactor and partly sent to the reactor operated in reduction

(#12). A small PSA is used to separate the required H₂ for the sulphur treatment of NG. NG pre-heating is carried out using the CO₂-rich stream from the fuel reactor and it is mixed first with IP steam from the steam turbine (to achieve a S/C ratio of 1.2) and later with recirculated H₂O/CO₂ to preheat the feed to 532 °C (#3) and achieve a final S/C of 1.83 ratio and CO₂/C ratio of 0.37 which is required to generate a syngas with M factor equal to 1.8 and a CH₄ conversion of 85% (#4). The syngas is cooled to ambient temperature and compressed to 55 bar before being converted in the MeOH synthesis unit. The MeOH reactor is cooled producing IP steam. The MeOH-rich stream (#6) is first separated from the main incondensable gases through a flash and a first distillation column and later fed to two distillation columns operated at 1.2 bar (feed #8) and 8.2 bar (feed #9) to achieve a final purity > 99%.

The design parameters for the heat recovery has been considered the same as for the H₂ production plant, therefore HP steam is generated at 92 bar and 485 bar (#19) and IP steam at 40 bar. LP steam (#19) at 6 bar is used in the reboilers of the distillation columns and partly for the export. The CO₂/H₂O-rich stream from the reactor(s) operated in reduction is cooled down, H₂O is separated and the remaining stream is compressed to 110 bar (96% purity due to the presence of some N₂ in the NG composition).

About 25% of incondensables gases are sent to the reduction reactor (#12). The CO₂/H₂O-rich stream from reduction (#14) can be varied to meet the desired specification of M for a proper methanol synthesis and for the NG humidification to avoid carbon deposition.

The overall mass balance and the main thermodynamic properties of each stream are listed in Table 9.

The comparison of the energy balance and performance indicators of the three MeOH production plants is reported in Table 10. Note that, compared to H₂ production, the size of the plant is significantly bigger (approximately 30 times). The 1s-ATR is more efficient than the 2s-

Table 8
Economic comparison for the H₂ production configurations.

	H ₂ -BC	H ₂ -HCC	H ₂ -MCC	H ₂ -CL _{PB}
Total plant cost, × item				
Fired Tubular Reforming (including pre-reforming)	22.76	22.76	22.44	
Water Gas Shift reactors	2.33	2.33	4.05	3.85
ZnO sulphur polisher	0.05	0.05	0.05	0.05
Pressure Swing Adsorption	6.29	6.29	5.21	8.63
Steam Turbine	3.18	3.18	3.09	3.19
Blowers/fan	0.24	0.24	0.23	0.06
CO ₂ compression		4.73	3.56	1.80
CO ₂ separation		55.94	25.49	
Syngas coolers	1.66	1.66	1.66	1.89
Chemical Looping reactor network				26.84
gas turbine				5.19
offgas compressor				3.58
Heat rejection unit	1.67	6.82	2.70	3.36
balance of plant	3.59	3.59	4.95	3.39
TPC	41.80	107.61	73.45	61.84
TOC	50.16	129.13	88.14	74.21
TASC	59.19	152.38	104.01	87.57
CCF × TASC	9.41	24.23	16.54	13.92
O&M fixed				
labor	2.00	2.00	2.00	2.00
maintenance	0.07	0.17	0.12	0.10
insurance	0.14	0.36	0.25	0.21
O&M variable				
catalysts	0.23	0.23	0.28	0.08
oxygen carrier				3.24
steam-to-import/export	0.02	−0.02		0.02
electricity	−1.03		−0.02	4.21
Natural gas feedstock	21.40	21.40	21.40	21.40
total annual cost	32.23	48.37	40.56	45.18
cost of hydrogen	\$/kg	1.63	2.45	2.06
	\$/Nm³	0.15	0.22	0.18
cost of CO₂ avoidance	\$/ton	0.00	95.58	70.64
				59.87

Fig. 3. Sensitivity analysis on the cost of CO₂ avoidance for H₂ production.

Fig. 4. Integration of chemical looping process for MeOH production.

Table 9

Mass balance of MeOH-CL_{PB} production as shown in Fig. 4.

#p	p bar	T °C	N kmol/s	m kg/s	MW kg/kmol	H ₂ O	Composition (%vol.)							
							N ₂	O ₂	H ₂	CO	CO ₂	CH ₄	C ₂₊	CH ₃ OH
1	70.0	15.0	4.08	73.55	18.02		0.01				0.02	0.89	0.08	
2	30.6	312.6	9.38	167.65	17.88	0.56			0.01		0.01	0.39	0.04	
3	27.5	532.5	13.68	285.12	20.84	0.58	0.01		0.01		0.12	0.27	0.02	
4	30.0	940.0	21.02	285.12	13.56	0.22			0.49	0.19	0.06	0.03		
5	56.0	56.7	32.40	424.88	13.11		0.01		0.60	0.19	0.11	0.08		
6	53.2	260.0	25.33	424.88	16.77	0.01	0.01		0.49	0.11	0.13	0.10		0.14
7	2.0	11.7	4.00	127.52	31.85	0.06					0.06			0.88
8	2.0	83.0	3.72	116.17	31.20	0.06								0.94
9	8.2	129.0	0.03	0.66	19.72	0.88								0.12
10	1.2	68.3	3.50	112.20	32.02	0.002								0.998
11	53.0	15.0	16.00	223.03	13.94		0.02		0.58	0.13	0.15	0.12		
12	25.0	26.6	5.61	85.68	15.27		0.02		0.55	0.12	0.18	0.12		0.01
13	25.0	350.0	5.53	85.51	15.46		0.02		0.54	0.13	0.19	0.12		0.01
14	24.2	1030.4	6.95	189.48	27.27	0.64	0.01				0.35			
15	33.7	207.0	2.64	72.00	27.27	0.64	0.01				0.35			
16	110.0	30.0	0.96	41.82	43.35		0.04				0.96			
17	25.0	466.0	15.47	446.39	28.85		0.79	0.21						
18	23.2	881.6	12.22	342.42	28.01		1.00							
19	40.0	342.2	5.21	93.93	18.02	1.00								
20	92.0	485.4	10.56	190.18	18.02	1.00								
21	40.0	262.7	1.27	22.81	18.02	1.00								
22	6.0	159.7	13.63	245.55	18.02	1.00								

Table 10

Energy balance and key performance parameters for the selected configurations for MeOH production.

Methanol Production		1s-ATR	2s-ATR	MeOH-CL_PB Chemical Looping
NG flow rate	kg/s	73.55	73.55	73.55
NG thermal Input	MW _{LHV, NG}	3418.67	3418.67	3418.67
MeOH flow rate	kg/s	118.34	112.46	112.20
MeOH flow rate	TPD	10224.77	9716.66	9694.36
Electricity prod/cons				
Fan/boosters	MW _{el}	−2.63	−6.12	−0.53
Gas turbine (comp + exp)	MW _{el}			5.85
syngas compressors	MW _{el}	−46.46	−53.66	−39.45
Air Separation Unit	MW _{el}	−71.50	−51.13	
CO ₂ compression				−3.32
Steam Turbine	MW _{el}	67.25	115.36	103.33
LP/HP pumps	MW _{el}	−2.79	−3.81	−3.26
oth. Auxiliaries	MW _{el}	−3.89	−3.67	−3.73
net electric power	MW _{el}	−60.02	−3.03	58.89
steam export (160 °C, 6 bar)	kg/s	91.92	54.04	67.37
MeOH efficiency	MeOH _{LHV} / NG _{LHV}	79%	75%	75%
Equivalent NG m _{NG,eq}	kg/s	71.18	70.97	68.02
Carbon conversion	mol _{MeOH} / mol _{C,NG}	80.3%	76.4%	76.2%
Eq. Ref. efficiency	MeOH _{LHV} / NG _{eq, LHV}	81.2%	77.4%	80.6%
Heat Rate	GJ _{LHV,NG} / ton _{MeOH}	27.77	30.43	29.94
CO ₂ specific emissions, E _{CO2}	kg _{CO2} /kg _{MeOH}	220	275	6

ATR, mostly because of the higher carbon conversion, which is explained with the higher fuel consumption required in the furnace due to the presence of N₂ in the oxidant stream (not present in the 1s-ATR). It is remarkable to notice that the 2s-ATR has lower electricity consumptions (3 MW_e vs 60 MW_e) mostly due to a lower amount of O₂ required for the reforming (−28.6%) and a higher electricity production through the steam turbine because a larger amount of high temperature heat is recovered to produce HP steam through the syngas coolers and flue gases. The 2s-ATR has a lower steam-to-export (steam consumption is higher compared to 1s-ATR). However, the 2s-ATR could represent a favourable solution in case the plant is located in more remote areas, where steam is not valuable, or electricity cost is excessively high.

The MeOH production efficiency of the MeOH-CL_PB plant is comparable with the 2s-ATR process and lower than the 1s-ATR. Despite the fact that N₂ from the oxidation reactor is delivered at high temperature, the overall thermal balance of the reforming section is mitigated by the lower temperatures of the gases at the outlet compared to 1s-ATR and 2s-ATR.

As discussed for the H₂-CL_PB process, the gas turbine specific work is very low (compared to a commercial natural gas fuelled gas turbine) related to the operating conditions and therefore the electricity production is modest. The syngas compressor duty in the MeOH-CL_PB is lower compared to the 1s-ATR and 2s-ATR, and this is associated with the lower volumetric flow rate because of the higher overall CH₄ conversion (96% vs 85%) due to the final temperature in the secondary reforming. In the MeOH-CL_PB, the syngas feed of the MeOH synthesis reactor contains 8% of CH₄ (vol.), whereas in the 1s-ATR the CH₄ content is 6.9%, and therefore no relevant effects on the yield of MeOH is expected, since the CH₄ normally does not participate in the reactions.

The ASU represents a large electricity consumption in both the 1s-ATR and 2s-ATR configurations due to the large amount of O₂ required for the autothermal reforming (respectively 80.8 and 56.8 kg/s of O₂). The electricity production from the steam turbine of the MeOH-CL_PB

process is 103.3 MW_e, higher than 1s-ATR (67.2 MW_e) and slightly lower than for the 1s-ATR (115.4 MW_e). Despite some cost for CO₂ compression up to 110 bar (3.3 MW_e), overall, the MeOH-CL_PB has a net electricity production of 58.9 MW_e. In terms of equivalent MeOH production efficiency, the MeOH-CL_PB is slightly lower than the 1s-ATR (−0.5 percentage points) and somewhat higher than the 2s-ATR (+3.3 percentage points). The two ATR configurations show respectively 220 and 275 kg_{CO2}/ton_{MeOH}, while in the case of the chemical-looping process the emissions are close to zero. In case of MeOH-CL_PB only 2% of the offgas is assumed to be lost to the atmosphere due to the switching operations resulting in 5.74 kg_{CO2}/ton_{MeOH}.

For the given mass and energy balances shown in the Table 9, overall 23 reactors are considered of 5.5 m internal diameter and 13.5 m length, in which 6 reactors are operated in oxidation, 2 reactors in purge, 4 reactors in reduction, and 6 reactors in reforming, while 5 spare reactors are present in the plant to assist any maintenance issue and ensure that the plant capacity is always higher than 85%. The total amount of oxygen carrier/catalyst required in the reactor is 4705 tons, which is assumed to be replaced every 2 years corresponding to the assumed OC lifetime. Therefore, compared to the 1s-ATR, the amount of material/catalyst required for the MeOH-CL_PB is 14.2 times more.

The chemical-looping process behaviour has been simulated for the given geometry and feed composition. Two cases have been considered: case (a) the OC active content is 3% and case (b) the OC active weight content is 20% (Ni supported on CaAl₂O₄). Increasing the Ni content in the OC increases the oxygen capacity of each single reactor and therefore, for given inlet conditions and reactor volume, the cycle time is longer and amounts respectively 550 s for case (a) and 1700s for case (b). In Fig. 5, the expected gas composition and gas temperature of the streams at the reactor outlets are shown for the two cases.

The case with the low Ni content (case a) does not exhibit relevant variations in the outlet temperature and it behaves effectively as a

Fig. 5. Gas conditions at the reactor outlet during the CLR in PBR using 3%wt. of NiO (over CaAl₂O₄) as for case (a) and 20%wt. of NiO (over CaAl₂O₄) as for case (b).

pseudo-steady state process, which is very beneficial from an operational point of view of the downstream process units. Moreover, the low Ni content could be beneficial for the OC lifetime/cost, particularly since this material is subjected to a low temperature difference over the cycle, approximately 100 °C for case (a), compared to about 400 °C for case (b). The dependence of the temperature rise on the OC composition has already been investigated and demonstrated in Noorman et al. (2007).

For case (a), the reactor unit (pressure vessel, high temperature valves and additional piping) may be subjected to excessive mechanical stress due to fatigue because of the short cycle time. This issue does probably not justify the use of a low OC content, however this decision is related to a specific appraisal in terms of reactor and process engineering, and the trade-off between cost of the reactor, cost of the OC, and control operation for a batch-based process.

For case (b), the authors have already demonstrated in Spallina et al. (2017a, 2015a,b) that the temperature of the gases and its fluctuation can be smoothed by operating multiple reactors which are carrying the same phase in parallel but with a phase displacement, as shown for the MeOH-CL_PB configuration in Fig. 6. This control strategy is beneficial for the other downstream processes because the flow rate, composition and temperature do not exhibit fluctuations after mixing as shown in Fig. 7: the temperature of the gas after oxidation and the products of reduction is almost constant (± 6 °C) while during the reforming there is a maximum temperature variation of only 40 °C over the entire cycle. This fluctuation is also slightly changing the expected stoichiometric M factor (as reported in equation 1), which is however within the desired range for more than 90% of the entire cycle.

4.4. Cost of methanol production

The economic analysis for the MeOH production is reported in Table 11. The overall TPC of the 1s-ATR and 2s-ATR is mostly represented by the cost of the syngas generation (respectively 25.2% and 39% of the total TPC) and the ASU (respectively 34.2 and 23.9% of the TPC). The other main units of the entire plant are very similar in terms of equipment and installation costs. Overall the TPC of the 2s-ATR is 5% higher than the 1s-ATR which is slightly lower than the difference estimated by Haldor Topsøe (+18% as reported in Kim Aasberg-Petersen et al. (2013)). This is partly explained by the fact that in the reference considered, the 2s-ATR configuration is assessed as 2 parallel syngas generation units of 5,000 TPD each while the 1s-ATR is one large unit of 10,000 TPD. Overall the costs are in line with the study published from the NETL (DOE/NETL, 2014a) about the baseline plant for MeOH production from which most of the cost database has been taken.

For the 1s-ATR and 2s-ATR the annual fixed and variable O&M costs

Fig. 7. Gas conditions chemical looping reactor outlet after mixing the streams coming from parallel reactors.

are mostly dictated by the cost of feedstock (47% of the total annual cost) and the main difference is the cost of electricity to import which is significantly higher for the 1s-ATR, as expected from the overall energy balance shown in Table 10. The final cost for MeOH generation ranges between 370 and 380 \$/ton_{MeOH} (the 2s-ATR is +4% higher) showing that two technologies are competitive.

In case of MeOH-CL_PB, the economic analysis shows a significantly lower TPC (-44% compared to 1s-ATR). The major reason is the absence of the ASU and a lower cost of the reactor network compared to the reforming section in the ATR plants. The overall chemical looping process including gas turbine, heat exchanger network, syngas compressor is 426 M\$ (about 17% lower than 1s-ATR). Also the BOP costs are lower due to the reduced auxiliary load. The fixed O&M mostly differ for the insurance which is calculated as fraction of the TASC. The cost for OC replacement has a relevant impact on the O&M variable cost, which is partly compensated by selling the additional electricity generated from the plant. Overall, the final cost of MeOH production is 304 \$/ton (> 17.5% lower than the ATR plants). Due to the combination of lower CO₂ emissions and lower MeOH cost of production, the resulting CCA is very negative (-303.1 \$/ton_{CO2}), which means that this plant is already economically attractive, regardless the cost associated to separate and compress the CO₂. Such negative price suggests considering business case-based CCUS processes, especially due to the fact that the CO₂ is delivered at high purity (> 96%) and overall the process presents a net production of electricity. The integration of a MeOH plant with a CCUS process will be investigated in a future work.

A sensitivity analysis has been carried out on the price of MeOH and CCA varying the cost of the chemical-looping reactors, the OC cost and lifetime and also the cost of generated electricity (from 0 to 105

Fig. 6. Reactor operation strategy for MeOH production.

Table 11
Economic comparison of the MeOH production configurations.

	1S-ATR	2s-ATR	MeOH-CL_PB
Total plant cost, × item	M\$		
Auto-thermal reforming + SC + syngas compressor	512.64	707.74	
Fired Tubular reforming + pre-reforming		122.58	
Air Separation Unit	694.85	507.86	
Methanol synthesis and separation	468.11	448.95	448.10
ZnO sulphur polisher	0.94	0.94	0.94
PSA	40.15	18.42	2.07
Steam Turbine	43.31	63.87	59.01
Blowers/fan	0.97	1.78	0.45
CO ₂ compression			6.23
Syngas coolers			5.62
Chemical Looping reactor network			311.15
gas turbine			89.71
offgas compressor			20.11
Heat rejection unit	35.85	35.58	36.01
balance of plant	231.98	221.33	158.80
Total Plant Cost, TPC	M\$	2028.81	2129.04
Total Overnight Cost, TOC	2434.57	2554.85	1365.82
Total As Spent Cost, TASC	2872.79	3014.72	1611.67
CCF × TASC	M\$/y	456.77	479.34
O&M fixed	M\$/y		
labour	4.50	4.50	4.50
maintenance	20.11	21.10	11.28
insurance	45.96	48.24	25.79
O&M variable	M\$/y		
catalysts	4.06	5.72	0.74
oxygen carrier			47.04
steam-to-import/export	0.21	0.01	-0.21
electricity	47.26	1.25	-24.29
Natural gas feedstock	599.98	599.98	599.98
total annual cost	M\$/y	1178.86	1160.14
cost of Methanol	\$/ton	368.94	382.07
cost of CO₂ avoidance (respect to 1s-ATR)	\$/ton_{CO2}	-	-303.10

\$/MWh). The results of the sensitivity analysis are shown in Fig. 8. The cost of MeOH production is always lower than the ATR configurations approaching 356.98 \$/ton in the worst-case scenario for the reactor network costs with a resulting cost of CO₂ avoidance of -55.8 \$/ton_{CO2}. In the case of combined high reactor cost (+300%) and low OC lifetime (1 year), the MeOH-CL_PB results are similar to those of the 1s-ATR (368.94 vs 372.5 \$/ton MeOH) with a CCA of 16.6 \$/ton_{CO2}.

5. Conclusions

The current paper has discussed the techno-economic advantages of integrating dynamically operated packed bed reactors in a chemical-looping-based process for the production of H₂ and MeOH with respect to state-of-the-art technologies.

In case of H₂ production, the chemical-looping based process is more advantageous than solvent-based technologies for CO₂ capture showing a minimal energy penalization and lower CO₂ avoidance cost ranging from 17–35% lower. In a long-term optimal scenario, the cost of CO₂ avoidance could reach potentially a low cost (< 30 \$/ton of CO₂), if the OC cost and lifetime would improve significantly compared to the current technology readiness level, as well as the design and the cost of the reactor network including all the auxiliary equipment such as valves and piping.

In case of MeOH production the chemical-looping based process presents only a slightly lower efficiency than the conventional technology due to a lower MeOH production rate, but higher than the two-stage reforming process because of the higher energy recovery. In terms of economics, the chemical-looping-based process is more attractive than competing technologies mostly because of the significantly lower plant costs due to the absence of the air separation unit. For MeOH production with the chemical-looping based process, the separation and compression units do not affect the final cost of the MeOH production, which results in about 17–20% lower costs than for the conventional cases. The combination of low CO₂ emissions and the low price of MeOH makes the cost of CO₂ avoidance negative, which could lead to a convenient business case for CO₂ utilisation.

The results of this work have identified the techno-economic and environmental advantages of a new chemical looping technology for

Fig. 8. Sensitivity analysis on the cost of CO₂ avoidance and the cost of MeOH production.

the production of H₂ and MeOH. Despite the very promising results further investigations are required to move toward the implementation and commercialisation of this technology. From a material point of view, more research should be carried out to further improve the stability and life time of the OC, preferably with lower costs metals that are environmentally benign low-cost, safe and stable than the current Ni-based OC. The experimental demonstration of the technology at larger scales as well as the full process operation and control would help to solve the existing technical challenges due to the dynamic operation and overall cost reduction of the technology. However, the expected performance presented in this work clearly justifies the research efforts required in the scale-up of this technology.

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