

# EFFICIENCY IMPROVEMENT THROUGH PROCESS INTEGRATION OF CHEMICAL LOOPING COMBUSTION AND MEMBRANE ASSISTED CHEMICAL LOOPING REFORMING

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## ABSTRACT

Chemical looping combustion and reforming are promising technologies for converting fossil fuel into power and hydrogen (H<sub>2</sub>). However, the temperature limitations in the reactor reduce their attractiveness. In the current study, an additional combustor is added to increase the turbine inlet temperature. Furthermore, three different process integration between CLC plant and membrane-assisted CLR plant are evaluated. Direct integration results in an efficiency of 53.08%. With further process integration, the plant can produce both power and H<sub>2</sub> with efficiencies 54.46% and 68.09%, respectively. The results show significant improvement in efficiency when compared to natural gas combined cycle and steam-methane reforming technologies.

**Keywords:** chemical looping combustion, membranes, reforming, hydrogen production, CO<sub>2</sub> capture, turbine inlet temperature

## NONMENCLATURE

### *Abbreviations*

CC	Combined cycle
CLC	Chemical looping combustion
CLR	Chemical looping reforming
COT	Combustor outlet temperature
MA-CLR	Membrane assisted chemical looping reforming
NGCC	Natural gas combined cycle
OC	Oxygen carrier
SMR	Steam methane reforming

## 1. INTRODUCTION

The anthropogenic carbon dioxide (CO<sub>2</sub>) emission in the atmosphere has risen beyond 415 ppm causing climate change [1]. Due to this, the Paris Climate Accord has vowed to limit the global temperature rise below 2 °C of the pre-industrial level [2]. The conventional power generation technologies such as natural gas power plants (NGCC) pose considerable energy penalty when integrated with a carbon capture facility. An amine-based capture system reduces plant efficiency by ~8%-points [3].

Chemical looping combustion combined cycle power plants (CLC-CC) has the inherent capacity to capture CO<sub>2</sub> with minimum penalty required for only compression [4]. The fuel and the oxidizer are treated separately using an oxygen carrier (OC), giving out a pure stream of CO<sub>2</sub> along with condensable water. However, due to the temperature limitations of the OC, turbine inlet temperatures in the range of 800-1200 °C are possible [5]. Therefore, the efficiencies obtained are unattractive in comparison to NGCC plants. This problem is addressed by introducing an additional combustor downstream of the air reactor in order to raise the turbine inlet temperature, which in turn is dependent on combustor outlet temperature (COT). Either natural gas or hydrogen (H<sub>2</sub>) can be burnt in the combustor. Burning of natural gas produces CO<sub>2</sub> in the combustor, which requires an additional capture facility. This will increase the energy penalty and capital cost of the plant. Hence, burning H<sub>2</sub> will be a suitable option. However, the production of H<sub>2</sub> is also accompanied by CO<sub>2</sub> emissions. Therefore, the

source of H<sub>2</sub> is critical in achieving high efficiencies with maximum carbon capture.

Conventional steam-methane reforming (SMR) is about 70% efficient with 80% carbon capture when using an amine-based capture system. This increases the H<sub>2</sub> cost by 40-100% [6]. Another promising method is the chemical looping reforming (CLR) which reduces the cost of H<sub>2</sub> significantly [7]. The attractiveness of the CLR process can be enhanced by using palladium based (Pd) membranes with high H<sub>2</sub> selectivity. The membranes are used to extract H<sub>2</sub> directly from the reforming reactor, which eliminates the need for water-gas shift and pressure swing adsorption units for separation. Cloete et al. [8] conducted an economic assessment of such a system. They reported the cost of H<sub>2</sub> can be as low as \$1.68 /kg at optimized operating conditions.

The current study presents the efficiency improvement strategies by integrating the CLC plant with an additional combustor with the membrane-assisted chemical looping reforming (MA-CLR). Four cases with different degree of plant integration are considered. The plant performance is evaluated based on the electrical and H<sub>2</sub> production efficiencies and compared to that of NGCC plant.

## 2. METHODOLOGY

### 2.1 Plant description

Fig 1 shows the process flow diagram of the CLC-CC plant with an additional combustor. The OC used in the CLC unit is NiO supported on NiAl<sub>2</sub>O<sub>4</sub>. The reduction and the oxidation reaction takes place in the fuel reactor and the air reactor, respectively. The air reactor outlet stream is at 1160 °C, which acts as the O<sub>2</sub> depleted oxidizer in the combustor. The H<sub>2</sub> fuel is injected and burnt with the oxidizer to raise the COT. For all the cases considered in this study, the COT assumed is 1416 °C. The outlet stream from the combustor is expanded in the gas turbine followed by heat recovery to produce superheated steam. This steam is expanded in the condensing reheat steam turbine assembly for additional power generation. The main plant specifications are listed in Table 1.

The source of H<sub>2</sub> in Fig 1 is MA-CLR plant represented in Fig 2. The natural gas is subjected to desulfurization at 324 °C to remove any sulfur compounds. The natural gas is then mixed with steam at a steam-to-carbon ratio of 1.75. This ratio is considered as higher ratios require more steam, which reduces the efficiency. The mixture is then pre-reformed to convert higher hydrocarbons at 490 °C using a nickel-based catalyst. This is to minimize

the coke formation in the process. The pre-reformed gas is further preheated before entering the fuel reactor of MA-CLR plant. As shown in Fig 2, the fuel reactor contains a series of Pd-membranes for H<sub>2</sub> extraction. In this process, the same OC (NiO-NiAl<sub>2</sub>O<sub>4</sub>) is used. The advantage of using the Ni-based OC is that the reduced nickel also acts as the catalyst for SMR and water-gas shift reactions. The retentate stream consisting of CO<sub>2</sub> and H<sub>2</sub>O is captured from the top of the reactor while the permeate stream consisting of pure H<sub>2</sub> is extracted through the membranes. The plant specifications are listed in Table 1.

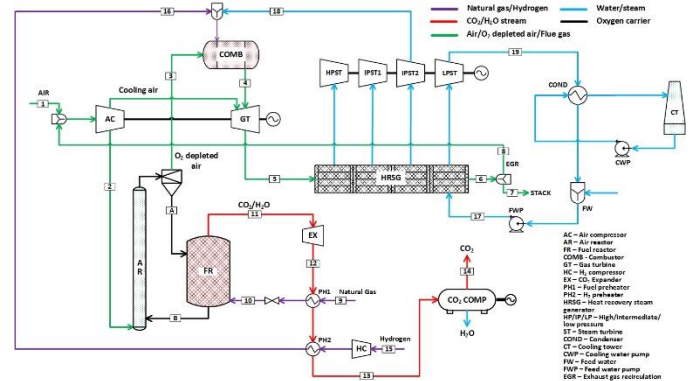


Fig 1 Schematic of chemical looping combustion combined cycle plant with the additional combustor

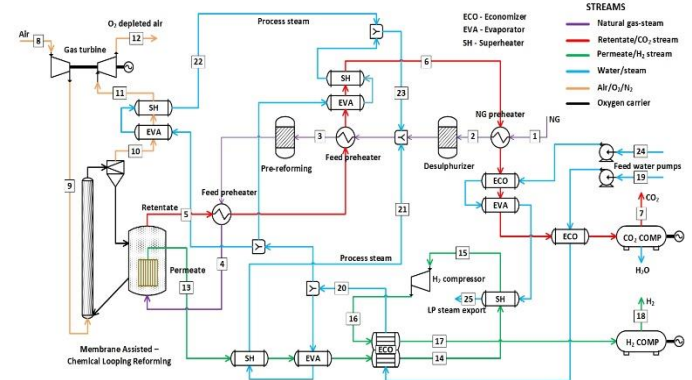


Fig 2 Schematic of membrane assisted chemical looping reforming plant

Three cases are considered in this study. Case 1 is the direct integration of the CLC and MA-CLR process by connecting the H<sub>2</sub> supply line to the combustor. Case 2 has slightly more degree of integration as shown in Fig 3. In this configuration, some part of the fuel reactor outlet stream of the CLC system is mixed with the natural gas required in the MA-CLR system maintaining steam-to-carbon ratio 1.75. The outlet stream from the AR of MA-CLR is expanded in the turbine followed by preheating the feed water. The retentate stream is used to produce saturated steam and then sent for compression whereas

the permeate stream is used to superheat the steam. This steam is sent to the steam cycle for additional power generation. The permeate is then used to further preheat the feed water before supplying into the combustor.

In Case 3 shown in Fig 4, the whole fuel reactor outlet stream of CLC plant is mixed with natural gas and injected into the fuel reactor of MA-CLR. Hence, CO<sub>2</sub> expander is not included in this configuration. The H<sub>2</sub> produced is more than that required in the combustor. Additional H<sub>2</sub> is compressed to high pressure and stored. Both the air reactor outlet streams of CLC and MA-CLR are mixed and sent to the combustor. The retentate stream is used to produce saturated steam and preheats part of feed water whereas the permeate stream is used to superheat the steam followed by preheating rest of the feed water.

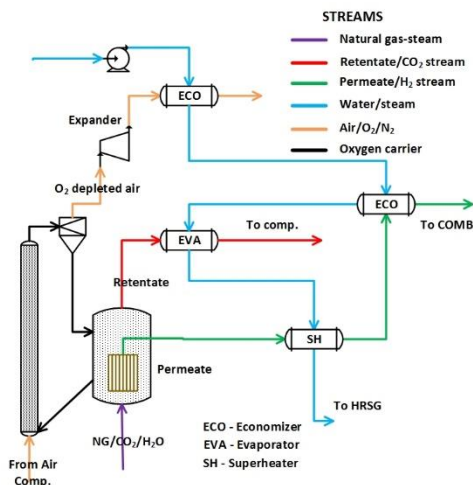


Fig 3 Schematic of case 2 (Only MA-CLR is shown)

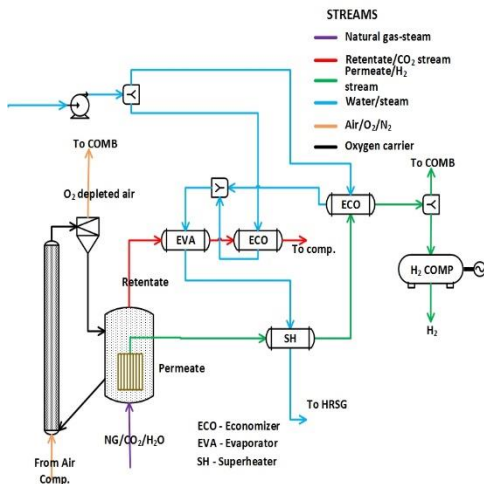


Fig 4 Schematic of case 3 (only MA-CLR is shown)

## 2.2 Process and reactor modeling

The fuel and the air reactor are modeled using RIGIBS module in Aspen plus. The properties are evaluated using Redlick-Kwong-Soave equation of state with Boston-Mathias alpha function. For the MA-CLR plant, a simple OD mass and energy balance model is used to determine the reactor behavior. The results of this model are coupled with the process simulations. The main assumptions used in developing the models are listed in Table 1.

Table 1 Plant specifications and main assumptions

CLC	
Reactor pressure drop, % inlet	5%
Air/H <sub>2</sub> compressor polytropic efficiency	92%
Gas/CO <sub>2</sub> turbine polytropic efficiency	92/85%
Comp/turbine isentropic efficiency	85%
Final CO <sub>2</sub> condition, °C/bar	30/110
MA-CLR	
Pre-reforming temperature, °C	490
Steam to carbon ratio	1.75
Reforming pressure, bar	20
Permeate pressure, bar	4
Final H <sub>2</sub> condition, °C/bar	30/150

## 3. RESULTS AND DISCUSSIONS

The main plants are validated and presented in our previous work [8]. The technical performance of the plant configurations is shown in Fig 5. The net electrical efficiency of the NGCC reference plant considered is 58.17%. The electrical efficiency obtained for case 1 and 2 is 53.08% and 54.62%, respectively. The corresponding energy penalty is 5.09 %-points and 3.55 %-points, respectively. On the other hand, the electrical efficiency for case 3 shown is 39.92% with an energy penalty of 18.25 %-points. This is the power-based efficiency without considering the additional H<sub>2</sub> produced. The global electrical and H<sub>2</sub> production efficiencies that show the net effect of power and H<sub>2</sub>, respectively, for this case are shown in Fig 6. The global H<sub>2</sub> efficiency obtained is 68.09%, which is similar to a conventional SMR plant with CO<sub>2</sub> capture. Additionally, the global electrical efficiency obtained is 54.46%, which is a significant improvement when compared to a conventional NGCC plant with CO<sub>2</sub> capture. Considering both power and H<sub>2</sub> produced, the overall efficiency obtained is 61.28%.

Table 2 shows the power consumption and generation from major plant components. The bulk of the power consumption comes from air compressors in all the cases. The consumption in case 1 and 2 is similar (38.9% and 39.2%, respectively) whereas the

consumption in case 3 is about 29.3%. This is because most of the fuel input is utilized in producing additional H<sub>2</sub>. The gas turbines produce bulk of the power in all the cases. Again, due to additional H<sub>2</sub> generation, the power produced by gas turbine in case 3 is 55.2%, which is significantly lower than in other cases. The power produced by CO<sub>2</sub> expander in case 1 and 2 is 4.32% and 2.5%, respectively. It is low in case 2 as some part of the FR outlet stream in CLC plant is mixed with feed natural gas to MA-CLR, maintaining a steam-to-carbon ratio of 1.75.

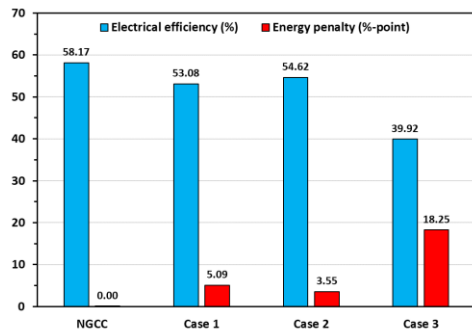


Fig 5 Performance comparison of different plant integration

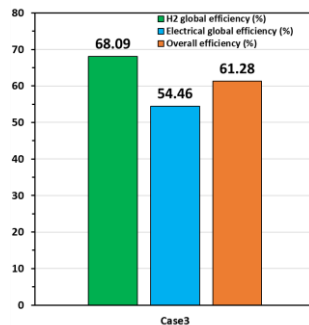


Fig 6 Performance of case 3 producing both power and H<sub>2</sub>

Table 2 Power generation and consumption based on fuel input

% of LHV	NGCC	Case1	Case2	Case3
Thermal input (MW)	765	998	983	1365
Air comp.	-36.7	-38.9	-39.2	-29.3
H <sub>2</sub> comp.	0	-1.15	-1.05	-1.91
CO <sub>2</sub> comp.	0	-1.78	-1.34	-0.79
Pumps	-0.62	-0.10	-0.10	-0.10
CO <sub>2</sub> pump	0	-0.04	-0.04	-0.04
Auxiliary	0	-0.63	-0.66	-0.52
Gas turbine	75	72.4	73.6	55.2
CO <sub>2</sub> expander	0	4.32	2.50	0
Steam turbine	20.48	18.92	20.91	17.42
Efficiency	58.17	53.08	54.62	39.92

#### 4. CONCLUSIONS

The current study deals with the efficiency improvement by process integration of a CLC-CC plant and a MA-CLR plant. Direct integration results in an efficiency of 53.08%. With further process integration, the plant can produce both power and H<sub>2</sub> with efficiencies 54.46% and 68.09%, respectively. The results show significant improvement in efficiency when compared to NGCC and SMR technologies.

#### ACKNOWLEDGMENT

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