

System analysis of natural gas combined cycle (NGCC) integrated with kinetics-based chemical looping syngas production

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System analysis of natural gas combined cycle (NGCC) integrated with kinetics-based chemical looping syngas production

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ABSTRACT

In this paper, we proposed an oxy-fuel natural gas combined cycle with carbon capture integrated with chemical looping (CO₂/H₂O) dissociation unit (CL) that produces syngas and fed back to the power plant to gain the efficiency point that is being lost due to carbon capture. The chemical looping CO₂/H₂O dissociation would produce syngas (CO and H₂ with methane reduction step in the redox cycle) from the recycled exhaust gas for additional power generation within the power plant. For developing an industrial scale CL unit, we developed the kinetics for methane reduced ceria and CO₂/H₂O splitting in an isothermal tubular micro-reactor for an operating temperature range of (900-1100°C) for different methane concentration and similar temperature and concentrations were adopted for oxidation which yielded to Avrami-Erofeev: AE3 model for both redox reaction with different reaction constants. A moving bed reactors system is developed representing reduction and oxidation reactors of CL unit and developed kinetics is hooked to the model in Aspen Plus with user-kinetic subroutine written in FORTRAN code. The CL model developed is integrated with the power plant layout proposed and investigated considering the effect of thermodynamics and the kinetics of redox reaction. It is found that the maximum non-stoichiometry (δ) reached during reduction is 0.29 instead of 0.5 when considered thermodynamics. The chemical looping unit efficiency obtained is 42.8% when considered kinetic-based CL unit compares to 64% for thermodynamic based CL unit. However, the electrical efficiency of the layout lowered as 50.9% for kinetic-based CL unit than 61.5% for thermodynamic based CL unit. Results also show that even with the redox kinetics, a decrease in energy efficiency penalty from 11.3% to 3.8% is observed yielding significant benefit of the proposed layout.

Keywords

Chemical looping, Redox kinetics, Experimental, Carbon capture and sequestration, Oxy-fuel power plant

1. INTRODUCTION

Most sought an approach to curb the carbon dioxide rise is carbon capture and sequestration and utilization (CCS&U). Mainly two-third of the CO₂ emissions are the result of fossil fuel used power production plants across the globe. CCS is adapted to retrofit the existing heavily invested fossil fuel plants to work on biomass as fuel or use the conventional carbon capture technologies such as post-combustion, pre-combustion or oxy-combustion. Though the CCS technologies maturity for large-scale capturing is still yet to demonstrate due to safety and economic feasibility leading to question in investing in viability for large-scale sequestration [1]. The mention reasons lead to investigate for alternate technologies for CO₂ utilization as a reactant and convert into fuel or hydrocarbons [2–4]. CO₂ splitting for CO production has received much interest after a successful demonstration of water splitting for hydrogen production using a two-step redox cycle with metal oxides as oxygen carriers. The idea conceived from direct dissociation of water which requires more than 2500 K temperatures. The high temperatures could be attained by solar energy. Later, the operating temperatures for CO₂/H₂O dissociation were proposed by metal oxide which has good oxygen-carrying capacity in a two step-redox cycle also termed as solar-thermochemical cycle [5,6]. The metal oxide also called as oxygen carrier take part in two separate reductions and oxidation reaction where solar-thermal reduction of metal oxide loses oxygen and become lower valence metal oxide. In the second step, the reduced metal oxide undergoes oxidation reaction with incoming CO₂/H₂O production CO/H₂ [7]. Here, a reduction

temperature higher than the oxidation one is the thermodynamic constraint for this process to be attainable, as shown in Figure 1.

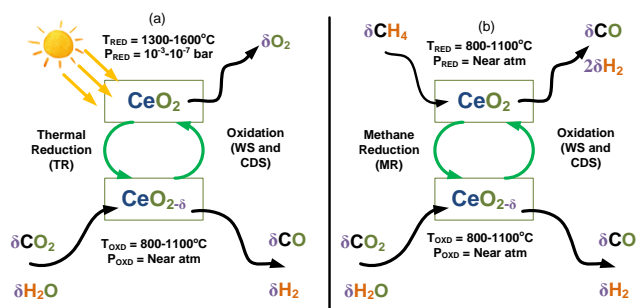
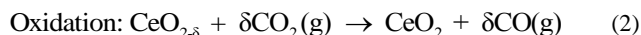
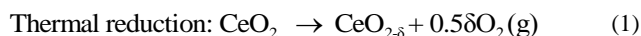


Figure 1: Conceptual scheme of the chemical looping syngas production through (a) solar thermal reduction and (b) methane reduction and corresponding splitting of water and carbon dioxide, usually present in waste gas from industrial applications

Among many investigated metal oxides for CO₂/H₂O dissociation redox reaction, ceria has shown great potential due to its higher oxygen transport capacity, electronic and ionic properties, and faster kinetics and it undergoes non-stoichiometric reaction without changing its microstructure at higher temperatures [8]. Following are the thermal reduction and CO₂ dissociation expressed as equation 1 and 2 and also represented in Figure 1a.



In thermochemical redox cycle, the oxygen release can be achieved either by heating ceria to a high temperature (1600°C) using concentrated solar irradiation (Eq. 1) or by reducing the metal oxide with CH₄, can also term as reactive-chemical looping redox cycle as equation (3).



The challenges associated with solar thermochemical dissociation to CO₂/H₂O to make fuel are related to achieving very high thermal reduction temperatures with the limitation of solar technology. Though this could be attained the two steps operate at different temperature creating a dynamic temperature swing along with pressure swing would limit the benefits if the process is not designed efficiently. With the fuel reduction step replacing the vacuum operated thermal reduction would eliminate the pressure swing operation making the two-step redox cycle to operate at near atmosphere. Very few numbers of studies reported the kinetics of methane reduction through some studies focused on the numerical equilibrium studies [9–12].

Based on the kinetics, it would be important to integrate the chemical looping unit into an oxyfuel power plant with carbon capture to investigate the feasibility and percentage efficiency point again with integration. One such study is reported based on an oxy-fuel power plant with 100% carbon capture [13]. But the study considered chemical looping unit (CL) based on the

thermodynamics of the two-step thermochemical looping. Since the reduction and oxidation kinetics having different reaction time it would be empirical to investigate the system based on the existing industrial scale reactor system to oversee the actual challenges associated with the proposed system that includes the kinetic behavior of gas-solid non-catalytic reactions.

Therefore, in the present study, a moving bed reactors system for CL unit is selected for both methane reduction and CO₂/H₂O splitting (oxidation) and developed model an oxy-fueled natural gas combined power plant with carbon capture.

2. EXPERIMENTAL

Isothermal redox cycles of CeO₂ commercial powders were performed in a horizontal tubular reactor in the temperature range of 900–1100°C. Methane (CH₄) was used for the ceria reduction to evaluate the reaction kinetics for commercial ceria and explore the maximum non-stoichiometric capacity (δ) achieved at a set-point temperature. Corresponding oxidation with different concentration of carbon dioxide in the oxidation step was performed with the aim to develop the reaction kinetics of reduction and subsequent oxidation of a methane-driven two-step chemical looping cycle with commercial ceria. The temperature swing is thus replaced by isothermal operation for developing the kinetics.

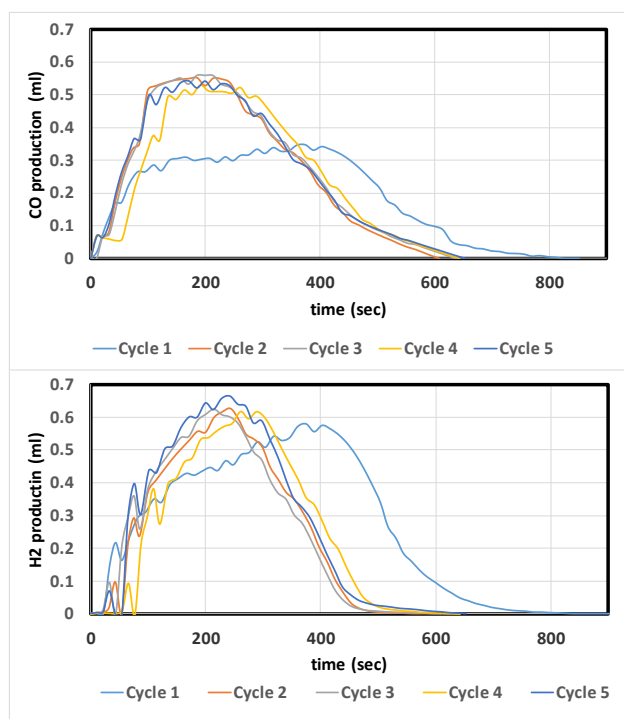


Figure 2 Instantaneous (a) CO and (b) H₂ production during isothermal reduction and oxidation at 1000°C reduction temperature with 50% CH₄

A Quadrupole Mass Spectrometer (QMS) (Hidden Analytical Inc.) was used to analyse the gas composition. Commercial ceria powder from Alfa Aesar (99.95% purity) was chosen for the reaction study. The sample was crushed and sieved to 32µm before the tests. A 250mg amount of ceria powder (m_{CeO2}) was

embedded in alumina wool and placed at the centre of the inner alumina tube. The total flow rate of gases into the reactor during both the reduction and the oxidation steps were maintained constant at 120Nml/min. During both the reduction and the oxidation, the mole fraction of the reactant gases (CH₄ and CO₂ respectively), were varied between 20% and 50%, balance argon. During the reduction, since one mole of methane leads to the formation of 2 moles of H₂ and one mole of CO, the molar flow at the outlet is higher than the inlet. However, as the production of 1 mol of CO leads to the consumption of 1 mol of CO₂, the total molar flow rate throughout the control volume remains constant during the oxidation cycle.

Each experiment was performed in a cycle of four steps. The first step included the ceria reduction step where the mixture of argon and methane was passed over the sample. Different concentrations of CH₄ (20-50%) was passed to evaluate the reduction mechanism. The readings of the QMS were observed to analyse for complete reduction of ceria. However, in the case of lower reaction rates at lower temperatures, the reactant gases were passes for 75 minutes to ensure enough reduction to study the corresponding oxidation. After completion of the reduction cycle, a purging stream of pure Ar was fed for 10 min, to remove the reactants and products present in the fixed bed from the previous cycle. The following step was the oxidation reaction where a mixture of Ar and different concentrations (20-50%) of CO₂ was sent for 15 min. The last step was the purging with pure Argon for approximately 10 min or until the QGA reading was stable enough to begin the next cycle, whichever is earlier. Isothermal redox cycles were performed at 900, 950, 1000, 1050 and 1100°C. The measure of H₂ and CO concentrations for the reduction cycle and the CO for the oxidation cycle at the outlet flow of the reactor allowed to extrapolate the reaction rate of the reduction and oxidation reactions respectively. However, for the reduction step, the methane splitting reaction can occur, which would give erroneous results from the reading of the hydrogen measurements due to the formation of H₂ and elementary solid carbon, which would be deposited inside the reactor. Indeed, this would be reflected by the corresponding oxidation, whereby the reaction kinetics would depend not only on the ceria oxidation but also on the Boudard reaction. For such a reduction reaction results is represented in Figure 2 where instantaneous CO and H₂ produced is represented for five cycles for an example case for 1000°C with 30% methane with the balance being argon.

Based on the experimental data, model fitting of the data to evaluate a kinetic model is performed by adopting the procedure reported in our earlier studies [14]. For reduction reaction all the models fitted to the experimental results, an average R² value of 0.97 was obtained for the Avrami-Erofeev: AE3 model, showing a good match. After the selection of the kinetic model, the evaluation of the kinetic parameters was carried out. Similarly, for oxidation, the AE3 model fits best with the experimental results and the average R² value obtained was 0.98, showing a good match. For both redox reaction, the reaction kinetics constants, activation energies and reaction order dependences on the reactants were evaluated with a 95% confidence level.

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3. SYSTEM ANALYSIS

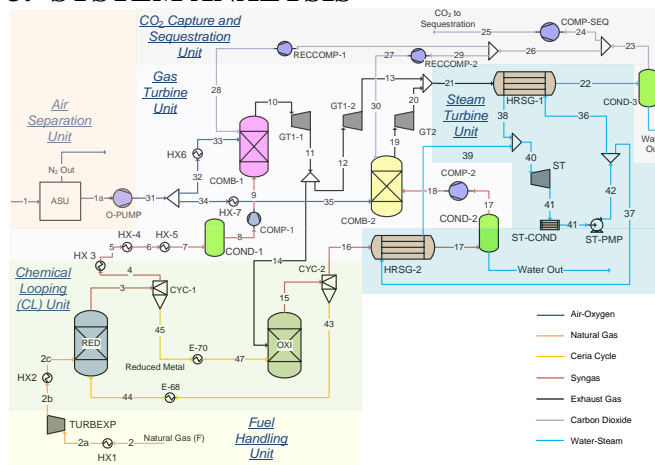


Figure 3 Process simulation flowsheet of MCLP-OXY-CC unit

The system proposed MCL-OXY-CC (as shown in Figure 3) comprises of air separation unit (ASU) that feeds pure O₂ to the combustion chamber that is supplied by natural gas making it an oxyfuel power plant, therefore, a part of CO₂ captured from the exhaust is recirculated back to the combustion chamber to reduce the elevated temperature due to oxy-combustion and maintain outlet gas temperature inlet turbine temperature (TIT). As ASU consume huge power which renders a 13% efficiency penalty. A part of the exhaust gas mixture (CO₂/H₂O) is sent to the oxidation reactor of the CL unit. The oxidation reaction would yield additional syngas fuel which is sent to the combustion chamber for additional power production which would also lower the incoming natural gas requirement. As the exhaust gases from the gas turbines are at high temperatures leading the gases to have a steam ranking cycle with a heat recovery steam generator (HSRG). As the plant is oxy-combustion based there would be minimal SO_x and NO_x, therefore, the exhaust gases can be cooled down to ambient temperature. Apart from two streams, one to oxidation reactor another to the combustion chamber for recirculation, remaining CO₂ is sent for storage after a compression of 110 bar.

Main equipment of the proposed layout is chemical looping (CO₂/H₂O) unit (CL). Natural gas is fed to the combustion chamber of the power plant at a supply pressure of 70 bars that comes from network and expanded to CL unit operating pressure which is neat atmospheric. The expanded natural gas is supplied to the reduction reactor (RED) where it undergoes partial oxidation of methane (POM) producing syngas. The operating conditions were selected to avoid complete combustion and methane cracking. This reaction is endothermic and needs heat in order to maintain the continuous reaction. Ceria reduction by methane is reported to occur above 900°C according to thermodynamics [13] but the reactor system is replaced with kinetics with a reactor temperature of 1000°C. Since a supplemental heat is required for reduction reactor an heat integration of combustion chamber of the power plant and reduction reactor is proposed with annular reactor design with inner reactor being reduction reactor of CL unit and annulus being combustion chamber providing excess heat [15]. More details of the system layout equipment operating conditions can be found in Farooqui et al. [13].

Hence, with the integration of CL unit, which recycles and converts a part of the exhaust gases to fuel, a net system efficiency improvement is expected for the conventional oxy-fired natural gas combined cycle with carbon capture of 100%. Model development of CL unit is described in detail below.

3.1 Moving bed reaction model

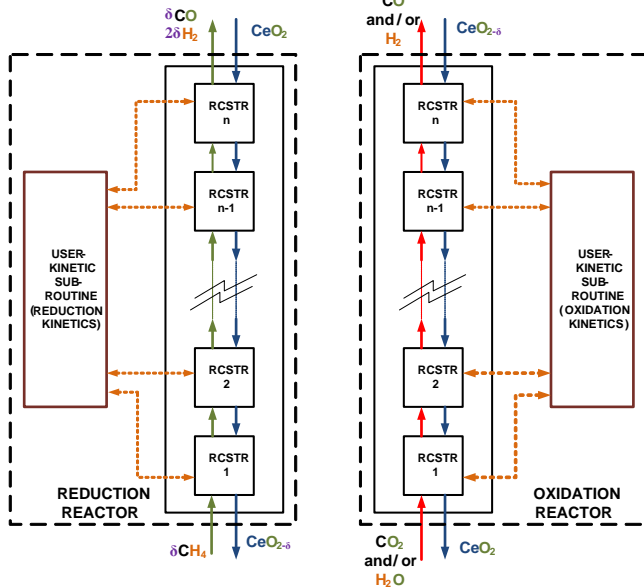


Figure 4 Moving bed reactor model for reduction and oxidation reactors in ASPEN Plus hooked with user kinetics written in an external FORTRAN Code

Figure 4 represents the schematic of counter-flow moving bed reactor system for reduction and oxidation reactor. In the reduction reactor (RED), ceria is introduced from the top by a hopper system (not shown) and it is reduced by incoming methane from the natural gas undergoing partial oxidation of methane producing syngas (CO+H₂) flowing up to the top of the reactor in a counter-current with respect to ceria flow. In the oxidation reactor, reduced non-stoichiometric ceria is fed from the top and the exhaust gas from the turbine (CO₂+H₂O) is fed from the bottom which moves up reacting with the metal oxide undergoing splitting reaction producing CO and H₂. The oxidized ceria is transported away from the bottom by a rotating conveyor system (not shown) to the reduction reactor. Since the oxidation reaction is exothermic, there will be a ΔT along the length of the reactor.

Each reactor is modelled as a series of rigorously continuous stirred reactors (RCSTR) interconnected in Aspen Plus. The RCSTR reactor is widely used in the simulation for multiphase having characteristic of the same temperature for all phases. The total volume of the reactor is a summation of all the RCSTR reactors connected in series. The reaction kinetics developed by model fitting the experimental data is written in FORTRAN as a user-kinetic subroutine for both reduction and oxidation and hooked to each RCSTR reactor in the moving bed reactor model in Aspen plus shown in Figure 4. There are few specific assumptions were considered in developed reduction and oxidation reaction in moving bed reactors such as a) all the RCSTRs in reduction reactor is modelled as isothermal and for oxidation reactor as adiabatic reactors. The residence time in each RCSTRs was calculated based on the bed volume with respect to ceria in-flow neglecting the volume change due to change in the

composition from reactions and lastly there is no change in the crystalline structure of ceria during redox recycling in the CL unit.

The number of RCSTRs selected for each reactor model relates to accuracy and time for simulation. With more number of RCSTRs the accuracy increases but the solution convergence is an issue as it is a two-point boundary condition problem [16]. Therefore, an iterative procedure is adopted, with increasing the number of the RCTRs is carried out until the relative change would result in a value lower than 0.25% change of the output of the moving bed reactor. The value of 0.25% was considered a good approximation to the reactor convergence while ensuring minimization of computation time by unnecessarily increasing the number of reactors in series. This results in 7 RCSTRs in series for reduction and 10 for oxidation as a good approximation.

In Aspen plus, Broyden solver was selected with 500 iterations for both mass and energy solvers with relative tolerance of 0.0001 and the PR-BM method which utilizes the Peng-Robinson cubic equation of state with the Bostone Mathias alpha function [17] is selected for the simulations.

4. RESULTS AND DISCUSSION

To improve on the thermodynamic evaluations reported by Farooqui et al [13], the GIBBS reactors for the RED and OXI were replaced by moving bed reactors model, as developed in the previous section was integrated into the described MCLP-OXY-CC unit and the energetic performance of the proposed plant layout was evaluated. As for the oxidation reaction, since the primary component of the exhaust comprises over 86% CO₂, the available water splitting kinetics were used alongside the newly developed CO₂ splitting kinetics by in-house experiments described in the previous section. Based on the experimental results, an isothermal reduction reactor at 1000°C was considered in the kinetic model. The heat integration and the annular combustion chamber concept was kept unchanged, whereby, the heat needed in the reduction reactor would be supplied from the heat generated in the combustion chamber. Additionally, the oxidation reactor was also considered a well-insulated adiabatic as opposed to a jacketed isothermal reactor at 1380°C considered during the thermodynamic analysis.

To explain the comparative results of the overall plant performance, the need to understand separately, the efficiency of the CL unit as a separate entity and the efficiency of the entire layout is crucial. In this regard, the efficiency of the CL unit, calculated as per equation (4).

$$\eta_{SCL} = \frac{(\dot{m}_{H_2} LHV_{H_2} + \dot{m}_{CO} LHV_{CO})_{red} + (\dot{m}_{H_2} LHV_{H_2} + \dot{m}_{CO} LHV_{CO})_{oxy}}{(\dot{m}_{CH_4} LHV_{CH_4} + (\dot{Q}_{red} - \dot{Q}_{oxd}) + \dot{Q}_{NG}) + (\dot{Q}_{spntr} - \dot{Q}_{sld})} \quad (4)$$

where \dot{Q}_{NG} is the heat necessary for heating the natural gas from after the turbo-expander to the condition necessary for the inlet to the reduction reactor; \dot{Q}_{red} is the heat requirement at the reduction reactor; \dot{Q}_{oxd} is the heat released from the oxidation reactor. Since the OXI is an adiabatic reactor, therefore, \dot{Q}_{oxd} accounts for the net heat needed for the system operations, including the heat needed for heating up the sweep gas and the inlet CO₂ and/or H₂O for splitting. \dot{Q}_{sld} represents the heat recovered from the solids

from the reduction reactor before it enters oxidation, while \dot{Q}_{spht} is the heat delivered to the solids for preheating. Since the exhaust of the turbine is directly sent to the oxidation unit, no heat-up of the same is necessary. Like before, the heat needed for heating of the solids and the heat required for cooling of the solids was not considered since an isothermal reactor system between the RED and the OXI was considered. However, it was ensured that no temperature cross-over takes place.

The results of the comparative evaluation of the performance of the CL unit from the thermodynamic to the kinetic evaluation is shown in Table 1. As can be seen, all other parameters being constant, the net energy rate content in the syngas formation in both the reactors is much less for the kinetic study. Indeed, for a lower non-stoichiometry, more specifically 0.295 obtained in the reduction reactor of 10 m³ volume, results in the production of a lower volume of syngas in both the reduction and oxidation reactors, unlike in thermodynamics, where a complete reduction of CeO₂ to Ce₂O₃ was assumed with an equivalent non-stoichiometry of 0.5. However, a lower non-stoichiometry also ensures the heating load of the reduction reactor to diminish, as compared to the thermodynamics levels. Nevertheless, the overall efficiency of the CL unit drops from 64.07% for ideal conditions to 42.88% for the evaluated operating conditions using developed reaction kinetic models. Also, it should be noted that the outlet temperature of the oxidized metal from the OXI drops to 1350°C as opposed to 1380°C obtained in the thermodynamic evaluation, requiring an additional heat removal of 4 MW. Nevertheless, such a high temperature of metal oxide in the RED, even though will considerably decrease the heat requirement of the reaction, might result in carbon deposition to occur as seen through experimental evaluations. Therefore, a detailed design optimization from multiple design perspectives needs to be assessed in further detail, which is beyond the scope of the present study.

Table 1 Comparison between the Thermodynamic and Kinetic Evaluation of the CL unit of the MCLP-OXY-CC unit

Parameter	Units	Thermo dynamic evaluation	Kinetic evaluation
Rate of Energy Content of Syngas from RED	MW	589.186	375.961
Rate of Energy Content of Syngas from OXI	MW	227.101	134.541
Rate of Net Energy in the Syngas Generated (H ₂ +CO)	MW	816.287	510.502
Q _{RED-IN}	MW	231.433	149.65
Q _{OXY-OUT}	MW	-4.44	0
Q _{NG}	MW	57.38	51.19
Rate of Energy Content in the Inlet Fuel (NG)	MW	989.667	989.667
η _{SCL}	-	64.07%	42.88%

However, unlike the efficiency of the CL unit, the plant efficiency depends not only on the net syngas generated in the CL unit but also on the total heat balance within the plant. Table 2 lists the comparison of the plant data for the thermodynamic assessment of the CL unit and the kinetic assessment of the same, all other

parameters being kept constant. Since the combustion is a very highly exothermic and spontaneous reaction, no kinetic study is necessary to evaluate the reactions occurring in the combustion chamber, and no other chemical reactions occur in the entire plant. Indeed, interesting to note the net efficiency of the plant increases slightly from 50.7% for the thermodynamic model to 50.96% utilizing a kinetic model of the CL unit. Multiple points of comparison between the two analyses of the same layout can be observed.

The heat requirement in the reduction reactor decreases due to a lower reaction extent, resulting in a lower non-stoichiometry of the reduced ceria. In addition, based on the concept developed for the oxidation reactor for the solar reduction-based cycle, an excess of exhaust gas was sent to the reduction reactor increase the net power produced from syngas generation via splitting in the OXI. Additionally, being directly from the gas turbine outlet at a pressure of 2 bars, a high gas temperature of 921°C at the inlet of the OXI was achieved. This results in the oxidized metal oxide temperature from the OXI to be at 1350°C as opposed to 1380°C for the thermodynamic layout.

Table 2 Plant Data Comparison of the MCLP-OXY-CC unit based on Thermodynamic and Kinetic Evaluation of the CL unit

Plant data	Units	MCLP-OXY-CC with thermodynamics	MCLP-OXY-CC with Kinetics
Fuel Energy Input, LHV (A)	MW _{th}	990.708	990.708
Net GT Output	MW	484.233	523.488
ST Output	MW	255.937	251.003
Gross Electric Power Output (B)	MW	750.206	774.491
ASU Consumption + O ₂ compression	MW	63.383	63.021
CO ₂ Capture and Compression	MW	19.222	18.021
Power Cycle Pumps	MW	3.287	3.10
Air/ Recycled CO ₂ Compression	MW	142.8797	153.61
Syngas Compressors	MW	17.1881	31.833
Total Parasitic Power Consumption (C)	MW	245.959	269.585
Net Electrical Power Output (D=B-C)	MW	504.247	504.906
Gross Electrical Efficiency (B/A*100)	MW	75.72%	78.18%
Net Electrical Efficiency (D/A*100)	%	50.70%	50.96%
CO ₂ Capture Efficiency	%	100%	100%
CO ₂ captured	t/h	178.658	178.658
Energy Output per tonne of CO ₂ Captured	MWh/t	2.822	2.826

On the other hand, the gas outlet temperature from the OXI drops considerably. Due to a countercurrent reactor configuration, as

well as from a lower reduction extent, the net exothermicity dropped considerably in the kinetic analysis than in the thermodynamic model. Hence, the gas outlet temperature noted was 1120°C, as opposed 1380°C for the thermodynamic layout assessment. This lowers the heat availability within the system. However, the outlet temperature from the RED increases as well from 905°C to 1000°C from the thermodynamic to the kinetic model. Besides, the composition of the syngas produced being varying significantly between the two models, the heat transfer characteristics are different as well.

The heat requirement in the RED being significantly lower for the kinetic model (by 80 MW), while the TIT remains constant, the net CO₂ recycled for temperature control in the COMB increases. Thus, the power produced in the GT increases. However, this also increases, accordingly, the auxiliary power consumption in the CO₂ recycling compressor for COMB1. Nonetheless, both the energy production and consumption from auxiliary for the COMB2 cycle decreases due to a lower non-stoichiometry generated from reduction, as can be seen from the results in table 2. Furthermore, a lower temperature of the syngas from the OX1 results in a lower steam generation in HRSG-2. Therefore, even though the gas expanded in GT1 and GT1-2 increases, the gas expanded in GT2 falls. The combined effect leads to a net drop in the power generated in the ST.

In summary, as can be followed from table 2, the net efficiency of the power plant is governed by the output from the GT, by far the single largest energy generating unit of the power plant. Even though the auxiliary consumption increases, the net efficiency of the power plant increases slightly for a lower non-stoichiometry resulting from integrating kinetics of methane reduction and corresponding oxidation of the reduced metal oxide by CO₂ and H₂O. Nevertheless, it needs to be highlighted that similar to the thermodynamic system, the kinetic layout is also a non-optimized one. Therefore, to develop a more even comparison between the maximum achievable efficiency by complete heat integration between the two layouts, a pinch analysis for the latter is required as well.

The pinch analysis of the layout using kinetic assessment of the CL unit is shown in Figure 5(b). A clear comparison to the pinch analysis of the layout using the thermodynamic assessment, as presented in Figure 5(a) can be drawn. Unlike the available 350 MW of high-temperature heat above 200°C for the thermodynamic layout, the system with the kinetics of the CL unit seems to be completely optimized without any heat available for further improvement of system performance. Therefore, the maximum achievable electrical efficiency is also limited to the present obtained value of 50.96%, as opposed to 61.5% achievable by system optimization of the thermodynamic layout. Nevertheless, even with kinetic limitations of the reduction and oxidation reactions, a reduction in the energy penalty, from 11.6 to only 3.8 percentage points is obtained, which would show the significant benefit of the proposed layout.

In fact, a net economic comparison with the thermodynamic layout was also performed, which are of interest due to the relative change in the sizes of the turbine and the compressors, resulting from a lower non-stoichiometry of ceria reduction. The total TOC of the plant was calculated as \$1224 million, around \$3
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million lower than the corresponding CAPEX calculated using thermodynamic evaluation of the layout. This change is however insignificant with respect to the other operating costs of the power plant as reported by Farooqui et al [13].

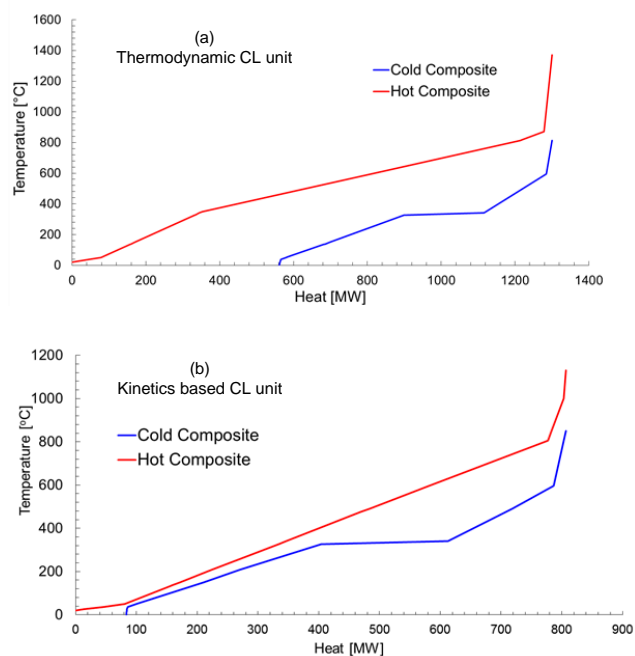


Figure 4 Pinch Analysis of the proposed MCLP-OXY-CC plant based on (a) thermodynamics model CL unit and (b) kinetics- based moving bed CL unit

5. CONCLUSION

Solar-thermochemical CO₂/H₂O dissociation redox cycles showed a promising technology to curb the global rise of carbon emission by converting CO₂/H₂O into syngas. But due to non-availability of solar energy, there is a transition for fuel reduction step in place of thermal reduction which operates at high temperatures and vacuum pressures. In the present study, we investigated the redox kinetics for commercial ceria considering methane for reduction that undergoes partial oxidation of methane producing syngas. For the oxidation step, part of the exhaust gases (CO₂/H₂O) from the oxy-fueled natural gas combined cycle power plant is fed to the oxidation reactor where splitting reaction takes place producing syngas. The produced syngas from both reduction and oxidation reactor is fed back to the combustion chamber. Since the reduction and oxidation kinetics paradigm has different reaction rates with different extent of reaction (non-stoichiometry) having the reactor sizing and hydrodynamics affecting the CL unit. Hence, experiments were performed to evaluate the kinetic model that fits the redox kinetics. Based on the different kinetic model fitting Avrami-Erofeev model with n=3: AE3 model fits both redox kinetics with different reaction parameters.

A moving bed reactors system is developed considered number of RCSTRs in series in Aspen Plus to mimic the moving bed behaviour of gas and solid in counter-flow direction with kinetics hooked using a user-kinetic subroutine. The developed CL unit is integrated with an oxy-fueled power natural gas combined cycle power plant and effect of kinetics on chemical looping unit performance and overall system layout performance is evaluated.

With kinetics, the maximum reaction extent relates as non-stoichiometry of ceria reached was 0.29 and the CL unit efficiency (η_{SCL}) was found to be 42.8% compared to 64% when thermodynamics is considered in CL unit. Similarly, the electrical efficiency of the whole plant was 50.9% with kinetics instead of 61% when thermodynamics is considered. A pinch point analysis is also performed in order to investigate if their system is tightly integrated for heat balance.

6. ACKNOWLEDGMENTS

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7. REFERENCES

- [1] D.Y.C. Leung, G. Caramanna, M.M. Maroto-Valer, An overview of current status of carbon dioxide capture and storage technologies, *Renew. Sustain. Energy Rev.* 39 (2014) 426–443. doi:10.1016/j.rser.2014.07.093.
- [2] Y.A. Daza, R.A. Kent, M.M. Yung, J.N. Kuhn, Carbon dioxide conversion by reverse water-gas shift chemical looping on perovskite-type oxides, *Ind. Eng. Chem. Res.* 53 (2014) 5828–5837. doi:10.1021/ie5002185.
- [3] J. Kim, C.A. Henao, T.A. Johnson, D.E. Dedrick, J.E. Miller, E.B. Stechel, C.T. Maravelias, Methanol production from CO₂ using solar-thermal energy: process development and techno-economic analysis, *Energy Environ. Sci.* 4 (2011) 3122. doi:10.1039/c1ee01311d.
- [4] S. Abanades, H.I. Villafan-Vidales, CO₂ and H₂O conversion to solar fuels via two-step solar thermochemical looping using iron oxide redox pair, *Chem. Eng. J.* 175 (2011) 368–375. doi:10.1016/j.cej.2011.09.124.
- [5] W.C. Chueh, C. Falter, M. Abbott, D. Scipio, P. Furler, S.M. Haile, A. Steinfeld, High-Flux Solar-Driven Thermochemical Dissociation of CO₂ and H₂O Using Nonstoichiometric Ceria, *Science* (80-.). 330 (2010) 1797–1801. doi:10.1126/science.1197834.
- [6] P. Furler, J. Scheffe, M. Gorbar, L. Moes, U. Vogt, A. Steinfeld, Solar Thermochemical CO₂ Splitting Utilizing a Reticulated Porous Ceria Redox System, *Energy & Fuels.* 26 (2012) 7051–7059. doi:10.1021/ef3013757.
- [7] P. Furler, J.R. Scheffe, A. Steinfeld, Syngas production by simultaneous splitting of H₂O and CO₂ via ceria redox reactions in a high-temperature solar reactor, *Energy Environ. Sci.* 5 (2012) 6098–6103. doi:10.1039/C1EE02620H.
- [8] V.M. Wheeler, J. Zapata, P. Kreider, W. Lipinski, Effect of non-stoichiometry on optical, radiative, and thermal characteristics of ceria undergoing reduction, *Opt. Express.* 26 (2018) 1238–1243. doi:10.1364/oe-26-10-A360.
- [9] H. Kong, Y. Hao, H. Jin, Isothermal versus two-temperature solar thermochemical fuel synthesis: A comparative study, *Appl. Energy.* 228 (2018) 301–308. doi:10.1016/j.apenergy.2018.05.099.
- [10] B.D. Ehrhart, C.L. Muhich, I. Al-Shankiti, A.W. Weimer, System efficiency for two-step metal oxide solar thermochemical hydrogen production – Part 1: Thermodynamic model and impact of oxidation kinetics, *Int. J. Hydrogen Energy.* 41 (2016) 19881–19893. doi:10.1016/j.ijhydene.2016.07.109.
- [11] S. Li, V.M. Wheeler, P.B. Kreider, W. Lipiński, Thermodynamic Analyses of Fuel Production via Solar-driven Non-stoichiometric Metal Oxide Redox Cycling—Part I: Revisiting Flow and Equilibrium Assumptions, *Energy & Fuels.* (2018). doi:10.1021/acs.energyfuels.8b02081.
- [12] S. Li, V. Wheeler, P.B. Kreider, R. Bader, W. Lipiński, Thermodynamic Analyses of Fuel Production via Solar-driven Non-stoichiometric Metal Oxide Redox Cycling—Part II: Impact of Solid–Gas Flow Configurations and Active Material Composition on System Level Efficiency, *Energy & Fuels.* (2018) acs.energyfuels.8b02082. doi:10.1021/acs.energyfuels.8b02082.
- [13] A. Farooqui, A. Bose, D. Ferrero, J. Llorca, M. Santarelli, Techno-economic and exergetic assessment of an oxy-fuel power plant fueled by syngas produced by chemical looping CO₂ and H₂O dissociation, *J. CO₂ Util.* 27 (2018) 500–517. doi:10.1016/j.jcou.2018.09.001.
- [14] A.E. Farooqui, A.M. Pica, P. Marocco, D. Ferrero, A. Lanzini, S. Fiorilli, J. Llorca, M. Santarelli, Assessment of kinetic model for ceria oxidation for chemical-looping CO₂ dissociation, *Chem. Eng. J.* 346 (2018) 171–181. doi:10.1016/j.cej.2018.04.041.
- [15] M.N. Khan, T. Shamim, Influence of Specularity Coefficient on the Hydrodynamics and Bubble Statistics of an Annular Fluidized Bed Reactor, *Energy Procedia.* 105 (2017) 1998–2003. doi:10.1016/j.egypro.2017.03.573.
- [16] C. He, X. Feng, K. Hoong, Process modeling and thermodynamic analysis of Lurgi fixed-bed coal gasifier in an SNG plant, *Appl. Energy.* 111 (2013) 742–757. doi:10.1016/j.apenergy.2013.05.045.
- [17] J. Fan, L. Zhu, P. Jiang, L. Li, H. Liu, Comparative exergy analysis of chemical looping combustion thermally coupled and conventional steam methane reforming for hydrogen production, *J. Clean. Prod.* 131 (2016) 247–258. doi:10.1016/j.jclepro.2016.05.040.