Solar fuels via two-step thermochemical redox cycle for power and fuel production

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ABSTRACT

With the issue of the rise of anthropogenic CO$_2$ with lead to global warming and rise of the primary energy demand, it requires strong measures for the energy transition and the diversification with renewables and existing fossil-based infrastructure. Prior to call for measures for carbon capture and sequestration, utilization of CO$_2$ would also be needed. In that sense, thermochemical redox cycles gained particular interest to produce synthetic fuel which leads to the production of other chemicals. Chemical looping CO$_2$/H$_2$O splitting (CL) via a two-step thermochemical pathway is composed of two redox reactions with a metal oxide. The first step is the reduction of metal oxides by losing oxygen and creating vacancies in the lattice at a higher temperature and becoming lower valence metal oxide. During the oxidation step, the reactant gases CO$_2$/H$_2$O reacts with the reduced metal oxide forming CO and H$_2$. A detailed mapping of different metal oxides has been investigated based on their oxygen carrying capacity and properties to under continuous redox cycles at temperature and pressure swing operation. After careful examination, ceria was selected for the application that can be available for large-scale CO$_2$/H$_2$O splitting.

In this present work, solar-driven thermochemical CO$_2$/H$_2$O splitting and methane-reduced chemical looping for CO$_2$/H$_2$O splitting for syngas production are investigated with the focus on non-structured reactors.

For solar-driven thermochemical looping cycle, an assessment of counter-current flow based moving bed reactor and fluidized bed reactors operating in different fluidizing regimes are assessed. It is moving bed reactor for both reduction and oxidation yield in high selectivity of the CO and H$_2$ with optimum reactor volumes while the similar yield could be achieved for bubbling fluidized bed reactor but the reactor volume required would be very high making it unfeasible. The reactor models were developed in Aspen plus and are validated from the literature. A sensitivity analysis revealed the CL unit is highly dependent on the reduction temperature and pressure. The analysis was extended by integrating the developed CL unit as an add-on unit to a 100 MW oxy-fired power plant with carbon capture. The efficiency of the plant was investigated considering only CO$_2$ splitting, only H$_2$O and mixture of CO$_2$ and H$_2$O as feed to the oxidation reactor of the CL unit. It resulted in maximum power output of 12.9 MW with solar to electricity efficiency of 25.4%. This additional power would bring down the efficiency loss due to carbon capture from 11.3 to 6%. To achieve this, the reduction reactor of CL unit need to operate at 1600°C and 10$^{-7}$ bar pressure. These conditions would need a huge solar field and the operation would be limited to only a few hours during the day without thermal storage integration. Techno-economic analysis revealed that the levelized cost of electricity 1100 $/MWh without including incentives or carbon taxation.

Subsequently, methane reduction of ceria as an alternative to thermal reduction was considered. At first, thermodynamic analyses of methane-driven CL unit were performed. From the analysis, it showed that the minimum temperature required was 900 with 50% excess of methane for reduction which yielded a CL unit efficiency of 62% with an optimum yield of CO and H$_2$. The CO$_2$/H$_2$O splitting in oxidation reactor was highly exothermic complete oxidation of
ceria, whereby a higher outlet temperature would considerably benefit the energetic efficiency of
the complete redox CL cycle. The variation of H₂/CO ratio at the output with respect to varying
input parameters including the composition of the gas to the oxidation reactor was studied to
specify the necessary operating conditions, while combined to subsequent chemical production
from the generated syngas.

Subsequently, methane-driven CL unit was integrated as an add-on unit to a 500 MW oxy-
fi red power plant. A comparative system performance with conventional natural gas combined
cycle, oxy-fired power cycle with carbon capture and the proposed plant was investigated. A
system efficiency and exergetic efficiency of 50.7% and 47.4 % were obtained respectively. The
system efficiency could be improved to 61.5%, subject to system optimization with pinch analysis.
A detailed techno-economic assessment revealed a specific overnight capital cost of 2455$/kW, the
levelized cost of CO₂ savings of 96.25 $/tonneCO₂, and an LCOE of 128.01 $/MWh. However,
with carbon credits of 6 $/tonneCO₂ the LCOE would drop below 50 $/MWh.

The methane-driven CL unit is later integrated as an add-on unit to a polygeneration plant that
produces electricity and dimethyl ether. The results showed that the plant can produce 103 MWe
and 2.15 kg/s of DME with energy and exergy efficiency of 50% and 44% respectively. The capital
investment required for the plant of $534 million. With the carbon credit price of $40/tonne of
CO₂, the current DME price of $18/GJ and the electricity price of $50/MWh would be achieved.
The costs resulted are due to air separation unit required for the oxi-fired power plant and it can
be reduced by replacing the air separation unit with oxygen transport membranes technology.

Since no comprehensive solid-state kinetic model exists in literature to describe the methane
reduction of commercial ceria, experiments were performed in a packed bed horizontal tubular
reactor within a temperature range of 900-1100°C. CO₂ splitting, being a more complex reaction
than water splitting was chosen to be studied for kinetic assessment as well, while water splitting
kinetics was obtained from the literature. Avrami-Erofe’ev (AE3) model was found to fit best to
both the cases, with respective activation energies being obtained as 283 kJ/mol and 59.68 kJ/mol
respectively. The order of the reaction was found as a relation between temperature and
concentration of the reactants. Since the analysis was performed based on thermodynamic approach,
but the heterogeneous reaction of metal oxide and reactant gases would limit to reach the
equilibrium during the reaction and would always depend on the type of reactor system chosen for
the CL application. Therefore, a moving bed reactor model developed considering the
experimentally obtained methane reduction and CO₂ splitting kinetics was incorporated to evaluate
the proposed power plant and polygeneration plant. A drop of 20% in the efficiency of the CL unit
was observed. However, due to thermal balance within the system, a similar thermal efficiency of
the overall plant was achieved as 50.9%. However, unlike the thermodynamic layout, no excess
heat was available to improve the system efficiency further. Besides CO₂ recycling and utilization,
the land and water footprint as a sustainability assessment criteria were analyzed for the proposed
layout. Both the land and water requirements increase by 2.5 times compare to conventional
natural gas combined cycle based power plant.
Furthermore, a polygeneration plant with power and dimethyl ether (DME) production has been investigated with kinetics based CL unit and found that the production of DME would drop from 2.15 kg/s to 1.48 kg/s and power from 103 to 72 MW. Therefore, kinetics has strong dependence and would reduce the production of power and DME by around 30% and it cost would increase by 30%.

Overall, integration of the CL unit as an add-on unit to the power plant is more suitable than polygeneration with respect to the cost compared to the existing market price.