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# Assessment of Hydrogen and Power Co-Generation Based on Biomass Direct Chemical Looping Systems

Calin-Cristian Cormos*, Ana-Maria Cormos, Letitia Petrescu

Babes – Bolyai University, Faculty of Chemistry and Chemical Engineering
11 Arany Janos, Postal code: RO-400028, Cluj – Napoca, Romania
cormos@chem.ubbcluj.ro

Biomass utilisation for energy production is very important in modern society. At EU level, by 2030, 27 % of the energy requirements are expected to be covered by renewable energy sources, biomass being one of the most important sources. Also, for the same period, the greenhouse gas emissions are expected to be reduced by at least 40 % below the 1990 level. In this context, carbon capture and storage (CCS) technologies are equally important for transition to low carbon economy. Chemical looping technique is a particular promising carbon capture option for reducing $CO_2$ capture energy and cost penalties.
This paper evaluates, from techno-economic and environmental perspective, the hydrogen and power co-generation based on biomass direct chemical looping systems with total decarbonisation of the fuel. As illustrative example, an ilmenite-based chemical looping system was assessed to generate about 500 MW net electricity with a flexible hydrogen output in the range of 0 to 100 $MW_{th}$ (based on hydrogen LHV). The capacity of evaluated plant concept to produce flexible hydrogen output is an important aspect for integration in modern energy conversion systems in which flexible operation scenario is of great importance due to greater integration of high time-irregular renewable energy sources (e.g. solar, wind). The carbon capture rate of evaluated concepts is almost total (>99 %). In addition, considering biomass (e.g. sawdust, agricultural wastes etc.) processing, the investigated power plant concepts have negative fossil $CO_2$ emissions. The performances are assessed for a number of case studies (including some benchmark cases) through process flow simulations. The simulation results are used to assess the main techno-economic and environmental indicators, e.g. energy efficiency, ancillary consumption, carbon capture energy and cost penalty, specific $CO_2$ emissions, capital and operation costs, cost of electricity, implication of hydrogen co-production on techno-economic and environmental performances etc.

## 1. Introduction

In modern society, enhancing primary energy supply sources and climate change prevention by reducing greenhouse gas emissions are objectives of great importance. Within this context, high energy efficient biomass conversion coupled with carbon capture and storage seems a potential attractive solution to hit the above targets (EC, 2014). Chemical looping is a promising energy conversion method with simultaneously carbon capture because $CO_2$ is inherently separated from the flue gas and no significant energy duty is required for the gas separation (Fan, 2010). This technology is attractive for reducing energy and cost penalties associated with carbon capture. Up to now chemical looping combustion (CLC) technique was applied mainly to gaseous fuels (e.g. natural gas, syngas) for heat and power generation. On the other hand, significant developments of this technology are needed for solid fuels utilisation (Lyngfelt, 2014) due to the process particularities such as ash removal together with oxygen carrier, longer residence time for high fuel conversion, oxygen carrier deactivation, operation at high pressure etc. But the current state of development of this technology looks very promising in delivering high energy efficiencies coupled with an almost total fuel decarbonisation rate (Cormos and Cormos, 2014).
This paper presents in details the biomass direct chemical looping concept as well as operational aspects such as mass and energy integration issues (e.g. Pinch Analysis was used to perform plant thermal integration). To illustrate the concept, an ilmenite-based chemical looping system was assessed to

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generate about 500 MW net electricity with a flexible hydrogen output in the range of 0 to 100 $MW_{th}$ (based on hydrogen LHV). The present work tackles the research gap of scale-up issues for chemical looping technology from current state of development - laboratory and pilot installations in the range of hundreds of kW up to 10 MW scale (Markström et al., 2013) to the full industrial size of hundreds of MW scale and the influence on main techno-economic and environmental performances. The plant designs were modelled and simulated using process flow modelling software (ChemCAD), the simulation results, in form of mass and energy balances, being used to assess the overall techno-economic and environmental performance indicators. For comparison reason, two benchmark power plant concepts were considered: a syngas-based chemical looping design (using also ilmenite as the oxygen carrier) and a Selexol®-based pre-combustion capture. The integrated techno-economic and environmental assessments show that biomass direct chemical looping has significant advantages compared with benchmark cases, the more important being the ability to process only biomass (an issue for conventional gasification processes), higher overall plant energy efficiency, lower energy and cost penalties for $CO_2$ capture, lower plant complexity and improved overall techno-economic and environmental performances.

## 2. Biomass direct chemical looping concept and main design assumptions

Solid fuel direct chemical looping scheme for hydrogen and power generation implies three gas-solid reactors operated in a cycle. In the first reactor (called fuel reactor), the fuel is oxidised with an oxygen carrier, usually a metallic oxide (ilmenite - $FeTiO_3$ in case of this paper) according to the following reaction:

$$Fe_2O_3 + Biomass\,(C_xH_yO_zN_mS_n) \rightarrow Fe/FeO + CO_2 + H_2O + N_2 + SO_2 \quad (1)$$

The gas stream from the fuel reactor is cooled down, the condense is removed and the $CO_2$ stream is dried using tri-ethylene-glycol (TEG) and compressed to 120 bar to be sent to storage. The reduced form of the oxygen carrier is partially reoxidised with steam to produce hydrogen in a steam reactor followed by total oxidation with air in an air reactor. The reactions for oxygen carrier reoxidation are presented below:

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2 \quad (2)$$

$$4Fe_3O_4 + O_2 \rightarrow 6Fe_2O_3 \quad (3)$$

Hydrogen produced in the steam reactor is cooled down for water condensation then a part it is used for power generation in a combined cycle, the rest being compressed for external customers. The conceptual layout of biomass direct chemical looping for hydrogen and power co-generation is presented in Figure 1.

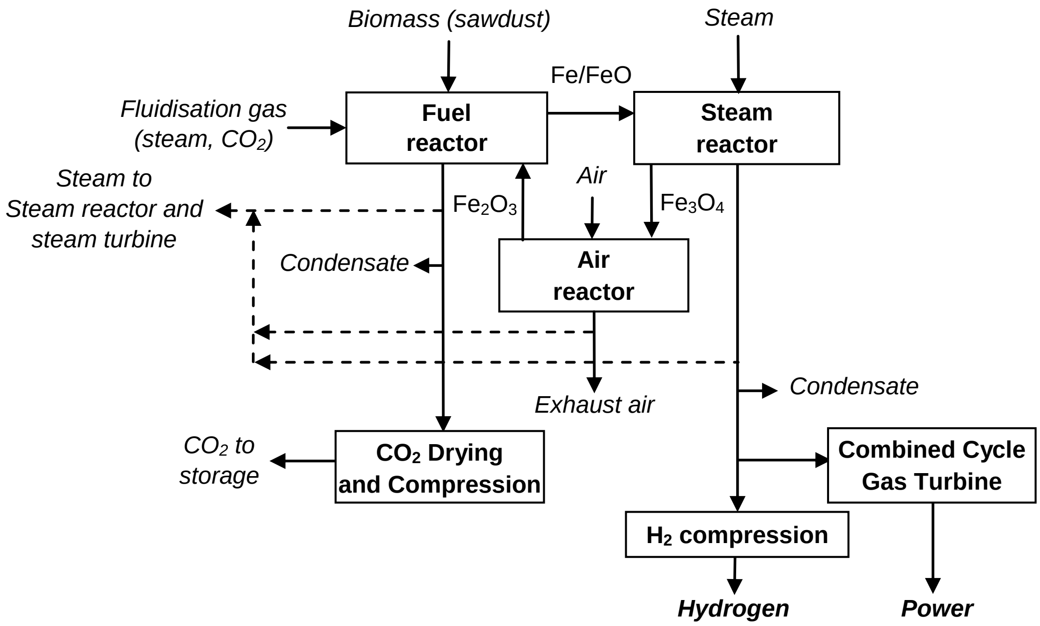



*Figure 1: Biomass direct chemical looping for hydrogen and power co-generation*

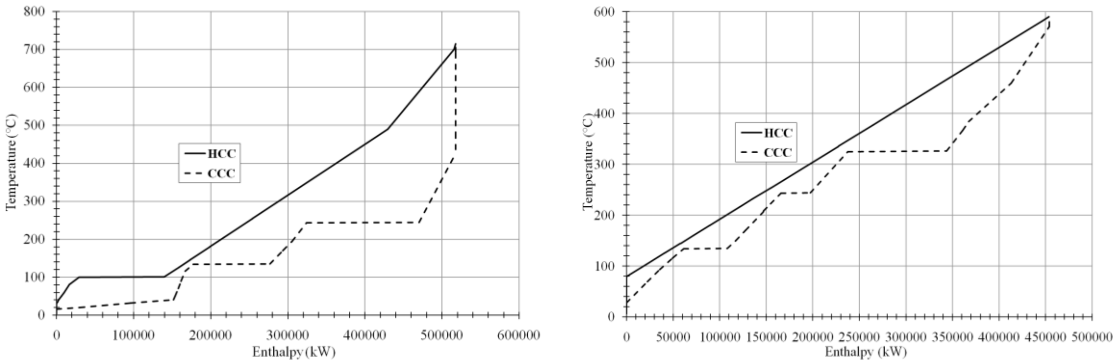
*Table 1: Main design assumptions*

| Plant unit | Parameter |
|---|---|
| Biomass direct looping (Case 1) | Ilmenite cycle @ 30 bar |
| Gasifier (Cases 2&3) | Shell type gasifier (dry fed & gas quench configuration) @ 40 bar |
| Air separation unit (Cases 2&3) | Oxygen purity: 95 % $O_2$; Power consumption: 225 kWh/t $O_2$ |
| Water gas shift (Case 3) | Sour shift; 3 catalytic beds; Steam/CO ratio: >2; CO conversion: >95 % |
| Carbon capture unit | Cases 1&2: Ilmenite (oxygen carrier) / Case 3: Selexol® (G-L absorption) |
| $CO_2$ drying and compression | Final delivery pressure: 120 bar; Drying solvent: TEG |
| Gas turbine | Type: M701G2; Net power output: 334 MW; 39.5 % efficiency |
| Steam cycle | Steam pressure: 120 bar / 34 bar / 3 bar |
| Condenser pressure | 46 mbar |
| Cooling water temperature | 15 $^oC$ |
| Heat exchanger $\Delta T_{min.}$ | 10 $^oC$ |
| HX pressure drop (ΔP) | 2-5 % |

As benchmark cases used to compare the biomass direct chemical looping, two IGCC plants with CCS were considered. The first option is also an ilmenite-based chemical looping but using syngas as fuel, the syngas is produced by coal and sawdust gasification (Cormos, 2012a). The second option is an IGCC design with pre-combustion capture using Selexol® (Cormos, 2012b). For all CCS cases, captured $CO_2$ stream has to comply with strict quality specifications (De Visser et al., 2008): >95 % $CO_2$; <2,000 ppm CO; <500 ppm $H_2O$; <100 ppm $H_2S$ and <4 % all non-condensable gases ($H_2$, $N_2$, Ar etc.). The hydrogen output has a purity higher than 99.95 %. All gas compositions are expressed in % vol.
The following plant concepts with carbon capture were evaluated in this paper:
Case 1 – Biomass (sawdust) direct chemical looping;
Case 2 – IGCC plant with syngas-based chemical looping using coal and sawdust as fuel;
Case 3 – IGCC plant with Selexol®-based pre-combustion capture using coal and sawdust as fuel;
All evaluated cases have an hydrogen-fuelled combined cycle based on M701G2 (Mitsubishi Heavy Industries) gas turbine. The main design assumption of evaluated plant concepts are presented in Table 1.

## 3. Results and discussions

All plant concepts were modelled and simulated using ChemCAD. The mathematical models are based on process flow modelling with detailed definition of the unit operations (e.g. looping cycle reactors, power block). The models were validated against available data (Fan, 2010). No significant differences were reported. The case studies were subject of process integration analysis using pinch technique for quantification of energy efficiency as presented by Anantharaman et al. (2013). As illustrative example, Figure 2 presents Hot and Cold Composite Curves for Case 1 (biomass direct chemical looping) for the two main plant sub-systems (the looping unit - Figure 2.a and the power block - Figure 2.b).
After modelling, simulation and thermal integration, the mass and energy balances of evaluated cases were used to assess the key techno-economic and environmental plant performances (IEA-GHG, 2003). The first evaluated operation scenario was considered only power generation. Table 2 presents the key technical and environmental indicators for evaluated cases.




*(a) Composite Curves for looping unit* *(b) Composite Curves for power block (CCGT)*

*Figure 2: Composite Curves for biomass direct chemical looping (Case 1)*

*Table 2: Key plant performance indicators (power generation only)*

| Main plant parameter | Units | Case 1 | Case 2 | Case 3 |
|---|---|---|---|---|
| Fuel flowrate | t/h | 268.60 | 175.19 | 178.90 |
| Fuel thermal energy (A) | $MW_{th}$ | 1,198.03 | 1,143.33 | 1,167.62 |
| | | | | |
| Gross power output (B) | $MW_e$ | 558.19 | 533.25 | 544.52 |
| Ancillary power consumption (C) | $MW_e$ | 48.37 | 98.44 | 114.25 |
| | | | | |
| Net power output (D = B - C) | $MW_e$ | 509.82 | 434.81 | 430.27 |
| Gross power efficiency (B/A * 100) | % | 46.59 | 46.63 | 46.63 |
| Net power efficiency (D/A * 100) | % | 42.55 | 38.03 | 36.85 |
| Carbon capture rate | % | 99.60 | 99.50 | 90.65 |
| $CO_2$ specific emissions | kg/MWh | 3.50 | 4.02 | 88.10 |

As can be noticed from Table 2, in terms of power generation only, the evaluated case studies generate about 430 – 510 MW net power with an electrical efficiency in the range of 36.8 – 42.5 % and specific $CO_2$ emissions in the range of 3.5 – 88 kg/MWh (coal-based power plants without CCS have specific $CO_2$ emission in the range of 750 – 900 kg/MWh). The most energy efficient plant concept is the one based on biomass direct chemical looping (Case 1) with about 4.5 net electricity percentage points higher than syngas-based chemical looping (Case 2) and about 5.7 points compared to Selexol®-based gas-liquid absorption (Case 3). The main reason for superior energy efficiency of chemical looping technique is lower plant complexity which implies lower ancillary power consumption (e.g. Case 1 does not need an ASU unit which is one of the major power consumer). Another important aspect is the carbon capture rate, both chemical looping designs (Cases 1 and 2) have almost total decarbonisation rate (>99 %) in comparison to 90 % for gas-liquid absorption design (Case 3). These results show the good potential of chemical looping technology to deliver high energy efficiencies simultaneously with almost total decarbonisation rate (Tong et al. 2014). In addition, direct solid fuel chemical looping option is fully flexible to process any kind of fuel (either fossil or renewable) which for the gasification plants is limited to 20 - 30 % biomass mixed with coal.
The second evaluated scenario is considering a combined production of hydrogen and power based on biomass direct chemical looping design (Case 1). Plant flexibility means the capability of the plant to change the produced energy vectors and to vary the plant output, whilst maintaining acceptable level of efficiency. For flexible co-production in range of 0 to 100 $MW_{th}$ hydrogen as evaluated in this paper, the gas turbine is gradually turned down to 85 - 90 % from the nominal load in order to displace an energy stream of hydrogen-rich gas which can be sent to external customers. Table 3 presents the variation of plant performance indicators with hydrogen output for Case 1 (biomass direct chemical looping).
As can be observed for co-production mode, the overall energy efficiency of the plant is increasing in the situation in which the ancillary power consumption is not changing significantly (see Table 3). This fact is very important and attractive for plant cycling, during low electricity demand from the grid the plant can produce mostly hydrogen which can be stored to be used either for peak loads or for other applications.

*Table 3: Key plant performance indicators vs. hydrogen output (Case 1)*

| Main plant parameter | Units | | Case 1 | |
|---|---|---|---|---|
| Sawdust flowrate (dried to 10 % wt.) | t/h | | 268.60 | |
| Sawdust thermal energy (A) | $MW_{th}$ | | 1,198.03 | |
| | | | | |
| Gross power output (B) | $MW_e$ | 558.19 | 529.15 | 500.31 |
| Hydrogen output (C) | $MW_{th}$ | 0.00 | 50.00 | 100.00 |
| Ancillary power consumption (D) | $MW_e$ | 48.37 | 48.81 | 49.34 |
| | | | | |
| Net power output (E = B - D) | $MW_e$ | 509.82 | 480.34 | 450.97 |
| Gross power efficiency (B/A * 100) | % | 46.59 | 44.16 | 41.76 |
| Net power efficiency (E/A * 100) | % | 42.55 | 40.09 | 37.64 |
| Hydrogen efficiency (C/A * 100) | % | 0.00 | 4.17 | 8.34 |
| Cumulative efficiency (E+C/A * 100) | % | 42.55 | 44.26 | 45.98 |
| Carbon capture rate | % | 99.60 | 99.60 | 99.60 |
| $CO_2$ specific emissions ($H_2$ + power) | kg/MWh | 3.50 | 3.11 | 3.00 |

*Table 4: Capital, specific investments and operation & maintenance (O&M) costs*

| Main plant parameter | Units | Case 1 | Case 2 | Case 3 |
|---|---|---|---|---|
| Total investment cost | MM € | 1,256.53 | 1,152.42 | 1,155.54 |
| Specific capital investment per kW gross | € / kW | 2,251.08 | 2,161.12 | 2,122.12 |
| Specific capital investment per kW net | € / kW | 2,464.66 | 2,590.34 | 2,685.61 |
| Total fixed O&M costs (year) | M€ / y | 48.28 | 41.12 | 38.95 |
| Total fixed O&M costs (MWh) | € / MWh | 12.62 | 12.61 | 12.06 |
| Total variable O&M costs (year) | M€ / y | 103.26 | 78.42 | 73.82 |
| Total variable O&M costs (MWh) | € / MWh | 27.01 | 24.04 | 22.87 |
| Total fixed and variable costs (year) | M€ / y | 151.54 | 119.55 | 112.77 |
| Total fixed and variable costs (MWh) | € / MWh | 39.63 | 36.65 | 34.93 |

The following economic indicators were calculated for the evaluated power plant cases: capital costs, specific capital investments, operational and maintenance (O&M) costs, cost of electricity, $CO_2$ removal and avoidance costs. The capital costs were calculated by cost correlations as presented by Cormos (2012b). The capital costs were estimated using a power law of capacity equation (see Eq(4)) in which material / energy flows were used as scaling factors.

$$C_E = C_B * \left(\frac{Q}{Q_B}\right)^M \tag{4}$$

where:
$C_E$ – equipment cost with capacity Q;
$C_B$ – known base cost for equipment with capacity $Q_B$;
M – constant depending on equipment type.
From the total capital (investment) cost, the specific capital investment (SCI) per gross or net power generation (€/kW) was calculated using Eq(5).

$$SCI\ \ per\ \ kW(gross/net) = \frac{Total\ \ investment\ \cos t}{Gross/\ Net\ \ power\ \ output} \tag{5}$$

Simulation results, in form of mass and energy balances for each evaluated cases, were then used for calculation of operational and maintenance (O&M) costs. These costs have variable and fixed components depending on the proportionality to the power output. Variable costs, proportional to amount of generated power, cover the following items: fuel, chemicals, oxygen carrier, solvents, waste disposal etc. Fixed operating costs, independent of the amount of generated power, cover: maintenance, plant depreciation, direct labour, administrative costs etc. Table 4 presents the plant capital costs, specific capital investments as well as fixed and variable operating and maintenance (O&M) costs for the investigated cases.

As investment cost indicators, the evaluated cases have total investment costs in the range of 1,152 to 1,256 MM €. The specific capital investments are in the range of 2,465 to 2,685 €/kW net. It can be observed that for biomass direct chemical looping case, the specific capital investment has the lowest value among the evaluated cases (about 4.8 percentage points less than syngas-based chemical looping design and 8.2 percentage points compared to Selexol®-based design). The O&M costs show a reversed trend, the highest value being for biomass direct chemical looping case (about 8 percentage points higher than Case 2 and 13.4 points higher than Case 3). This is mainly due to oxygen carrier make-up despite of the fact that Case 1 has the highest energy efficiency from all investigated cases.

$CO_2$ removal and avoidance costs are important parameters when assess carbon capture technologies (lowest values being more favourable). These indicators are using the levelised cost of electricity (LCOE) in a power plant with CCS compared with cost of electricity without CCS as well as specific $CO_2$ emissions in both cases. These costs are calculated using Eq (6) and Eq (7).

$$CO_2\ \ removal\ \cos t = \frac{LCOE_{with\,CCS} - LCOE_{without CCS}}{CO_2\ \ removed} \tag{6}$$

$$CO_2\ \ avoided\ \cos t = \frac{LCOE_{with\,CCS} - LCOE_{without CCS}}{CO_2\ \ emissions_{without CCS} - CO_2\ \ emissions_{with\,CCS}} \tag{7}$$

*Table 5: Capital, specific investments and operation & maintenance (O&M) costs*

| Main plant parameter | Units | Case 1 | Case 2 | Case 3 |
|---|---|---|---|---|
| Levelised cost of electricity (LCOE) | € / MWh | 78.41 | 77.08 | 76.45 |
| $CO_2$ removal cost | € / t | 27.35 | 26.41 | 26.75 |
| $CO_2$ avoided cost | € / t | 32.92 | 31.13 | 34.18 |

Table 5 presents the $CO_2$ removal and avoidance costs as well as cost of electricity for investigated cases. As reference power plant without CCS, a Shell-based IGCC plant was considered with a levelised cost of electricity of 54.13 € / MWh and 741 kg/MWh $CO_2$ specific emissions (IEA-GHG, 2003).
The levelised cost of electricity shows a moderate increase for chemical looping designs (Cases 1 and 2) compared to Selexol® design (Case 3) mainly due to oxygen carrier make-up cost. This is more prominent for biomass direct looping case with about 2.5 percentage points (more oxygen carrier needs to be replaced for solid fuel looping compared with syngas-based design due to the need for ash removal).

## 4. Conclusions

This paper focuses on hydrogen and power co-generation based on biomass direct chemical looping. The analysis demonstrates that direct solid fuel chemical looping is a very promising option to increase overall energy efficiency (5.7 net percentage points compared to gas-liquid design and 4.5 points compared to syngas-based looping design) as well as a reduced capital cost penalty (4.8 - 8.2 percentage points lower specific investment cost) for carbon capture with an almost total decarbonisation rate (>99 % vs. 90 % for Selexol®-based option). O&M costs show an increase of about 8 to 13.4 percentage points compared to benchmark cases for biomass direct looping due to oxygen carrier make-up. Hydrogen and power co-generation capability is an attractive feature to boost energy efficiency and plant flexibility (load following).

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