



A comparative simulation study of power generation plants involving chemical looping combustion systems



Moises A. Petriz-Prieto^a, Vicente Rico-Ramirez^{a,*}, Guillermo Gonzalez-Alatorre^a,
Fernando Israel Gómez-Castro^b, Urmila M. Diwekar^c

^a Instituto Tecnológico de Celaya, Departamento de Ingeniería Química, Av. Tecnológico y García Cubas S/N, Celaya, Guanajuato 38010, Mexico

^b Universidad de Guanajuato, División de Ciencias Naturales y Exactas, Departamento de Ingeniería Química, Noria Alta S/N, Guanajuato, Gto. 36050, Mexico

^c Vishwamitra Research Institute, 368 56th Street, Clarendon Hills, IL 60514, USA

ARTICLE INFO

Article history:

Received 4 March 2015

Received in revised form

28 September 2015

Accepted 3 October 2015

Available online 14 October 2015

Keywords:

Chemical looping combustion

Power generation plants

Thermal efficiency

Economic evaluation

ABSTRACT

This work presents a simulation study on both energy and economics of power generation plants with inherent CO₂ capture based on chemical looping combustion technologies. Combustion systems considered include a conventional chemical looping system and two extended three-reactor alternatives (exCLC and CLC3) for simultaneous hydrogen production. The power generation cycles include a combined cycle with steam injected gas turbines, a humid air turbine cycle and a simple steam cycle. Two oxygen carriers are considered in our study, iron and nickel. We further analyze the effect of the pressure reaction and the turbine inlet temperature on the plant efficiency. Results show that plant efficiencies as high as 54% are achieved by the chemical looping based systems with competitive costs. That value is well above the efficiency of 46% obtained by a conventional natural gas combined cycle system under the same conditions and simulation assumptions.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

It has been well documented that electric power plants using fossil fuels produce more than one third of the global carbon emissions (see Fig. 1; USEPA, 2015). As a result, there is a growing research interest in developing approaches for CO₂ mitigation from power generation. These approaches include (i) the use of renewable energy sources, (ii) the use of low-carbon fuels such as natural gas, (iii) the improvement of plant efficiencies and (iv) the capture of CO₂ from the energy systems.

A conventional process for CO₂ capture through amine absorption in a natural gas power plant based on current state of the art technologies reduces the thermal efficiency by about 10% (Brandvoll and Bolland, 2004). The challenge is then to generate alternative processes for CO₂ mitigation with a smaller penalty in efficiency.

The implementation of chemical looping combustion (CLC) systems emerged as one of the most promising techniques for CO₂ capture in power plants; CLC has the potential to separate CO₂ with only small penalties in plant efficiency. In the conventional version

of a CLC (see Fig. 2), combustion takes place into two separate reactors (oxidation and reduction reactors), using a metal that acts as an oxygen carrier; then, separate streams of exhaust air and CO₂ are obtained. Therefore, the oxygen carrier avoids direct contact of fuel and combustion air, and the CO₂ is then inherently separated from nitrogen; no additional process operations are needed for CO₂ separation.

State of the art technologies for natural gas fired combined cycles (NGCC) without CO₂ capture achieve plant efficiencies from 55–60%. Following the report by Brandvoll and Bolland (2004), and assuming a penalty of 10% due to CO₂ capture and compression, NGCC technologies can still reach an efficiency of 45–50%. As a result, to compete with current commercially available technologies, a CLC based power generation plant has to achieve net low heating value (LHV) plant efficiencies of 50% or higher.

This work presents a simulation study that provides a comparison among several configurations including the incorporation of CLC systems into various state-of-the-art technologies for power generation. The comparison also includes a conventional NGCC system. Two basic criteria are used for comparison: The net LHV plant efficiency and an economic assessment including the estimation of the capital investment, and operation and unit production costs. Additional results include the models sensitivity to the pressure in the reactors, the oxygen carrier and the gas turbine inlet

* Corresponding author. Tel.: +52 461 611 7575×5579; fax: +52 461 611 7744.
E-mail address: vicente@iqcelaya.itc.mx (V. Rico-Ramirez).

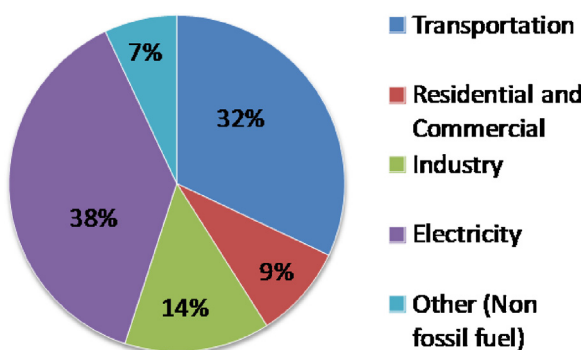


Fig. 1. 2013 global CO₂ emissions from fossil fuels (USEPA, 2015).

temperature (TIT). Then, this paper reports our results with respect to the technical and economic feasibility of CLC based power generation plants.

2. Background

The literature on CLC systems is extensive. Current research in CLC configurations focuses on the practical implementation of the various components of the system. Several studies have reported advances on novel extended CLC configurations and related simulation studies about their performance in power plants and other combustion processes.

2.1. Fundamentals of CLC and novel extended systems

The fundamentals of the chemical looping concept and its several reactor configurations have been extensively addressed. Some of the classical literature includes the works by (Ishida and Jin, 1996, 1997, 2001) and Jin and Ishida (2000). Those works provide the basic foundations of CLC and its potential application to gas turbine power generation cycles. Further developments consider the use of alternative fuels for the chemical looping combustor (Jin and Ishida, 2004). In fact, a coal-direct chemical looping (CDCL) process has been recently patented. Such a system converts pulverized coal feedstock to fuel in one integrated system without additional gasification, and allows both electricity and/or hydrogen production (Kim et al., 2013; Connell et al., 2013; Adanez et al., 2014).

The chemical looping concept has been extended to consider reforming (Chemical Looping Reforming, CLR), where complete oxidation of the fuel is prevented by using low air to fuel ratio (Ryden et al., 2006). Further, the simple CLC configuration has been extended to include a third reactor that favors the simultaneous generation of hydrogen. In this work we consider two instances of

those extended CLC configurations: The exCLC system described by Wolf and Yan (2005) and the CLC3 system proposed by Chiesa et al. (2008). Those configurations will be discussed in detail in Section 3 of this work.

2.2. Simulation and performance in power generation systems

Similar to our work, several authors have performed simulation studies and sensitivity analysis of various parameters, fuels, oxygen carriers, CLC configurations and power plant cycles. Most of the works include estimation of the net LHV plant efficiency. Among these works, Wolf and Yan (2005) studied a combined cycle and a steam injected gas turbine cycle (STIG) with both simple CLC and extended CLC (exCLC) configurations, finding efficiencies as high as 52%. Brandvoll and Bolland (2004) and Olaleye and Wang (2014) considered CLC-Humid Air Turbine (HAT) configurations reaching higher efficiency values (56%). Consonni et al. (2006) presented a comprehensive parametric analysis of CLC-combined cycle configuration using natural gas as fuel and iron as oxygen carrier. Gupta et al. (2006) focused their analysis in the CLR system, achieving hydrogen conversions as high as 82%. Jordal and Gunnarsson (2011) propose process configurations for handling unconverted fuel remaining in the captured CO₂-rich stream of a CLC system. Finally, recent developments report novel configurations which combine chemical looping combustion, the calcium-looping process, hydrogen production and the integrated gasification combined cycle for power generation (Fan and Zhu, 2015; Zhu and Fan, 2015; Zhu et al., 2015); simulation studies report the technical feasibility and economic potential of such combined/integrated systems.

2.3. Contribution of this comparative simulation study

Our study includes a conventional chemical looping (CLC) and its extended version (exCLC) for simultaneous hydrogen production, as well as the three-reactor configuration known as the CLC3 system. The power generation cycles used for our analysis include a combined cycle with steam injected gas turbines, a humid air turbine cycle and a simple steam cycle (SC). For the purpose of comparison, a conventional natural gas combined cycle (NGCC) was also simulated. We analyze the operation, investment and unit production costs as well as the net plant efficiency, and study the effect of the pressure on the system reaction and the material flows that control the turbine inlet temperature (TIT). To the best of our knowledge, there is not a single work which compares and analyzes the various configurations resulting from the use of the three CLC systems and the three power plant configurations studied in this paper. Therefore, we believe our paper contributes to the existing literature on the topic. In particular, results about the CLC3 system are quite limited.

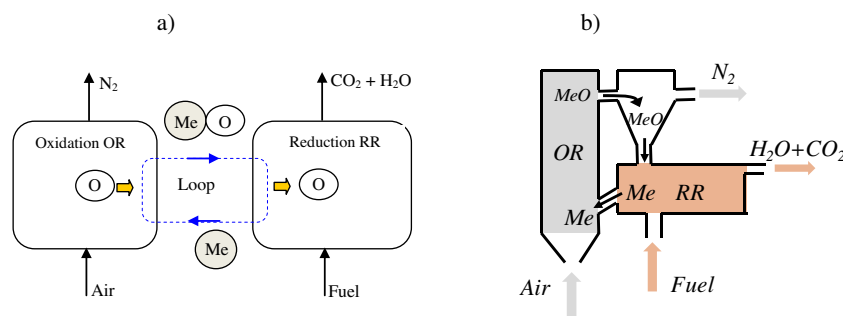


Fig. 2. Chemical looping combustion configuration. (a) The concept. (b) The system.

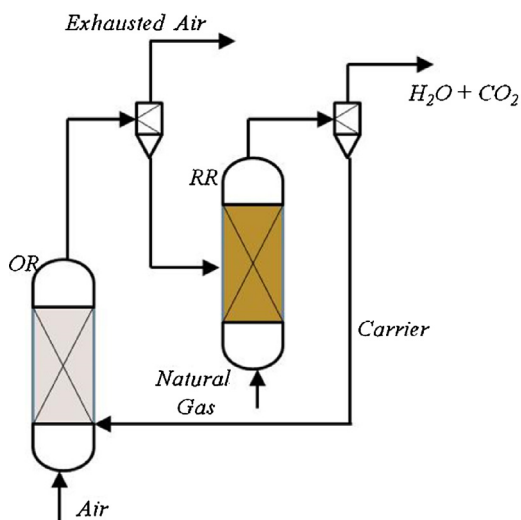


Fig. 3. A conventional two-reactor chemical looping combustion configuration.

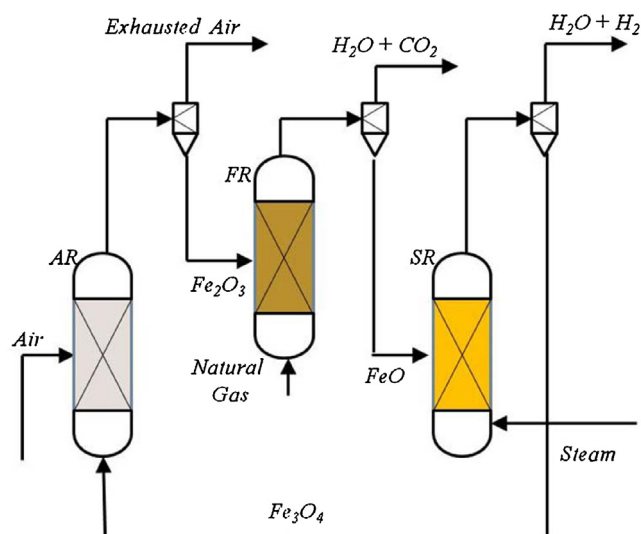


Fig. 5. CLC3 configuration with hydrogen production.

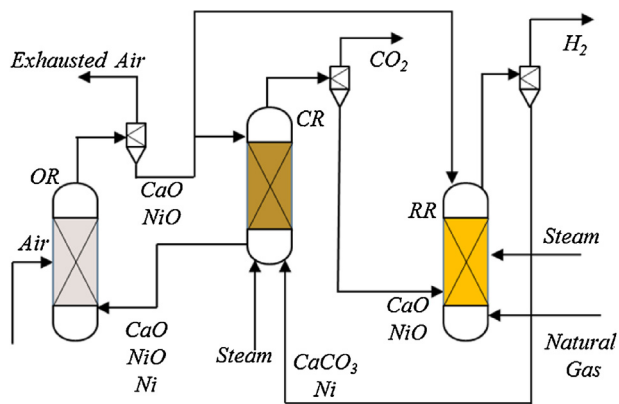


Fig. 4. The extended CLC configuration of Wolf and Yan (2005).

3. Chemical looping systems and power plant configurations

Fig. 3 presents a conventional CLC configuration including the oxidation (OR) and reduction (RR) reactors and two cyclones for solid–gas separation. Inlet streams include air, fuel (natural gas in most of the cases) and the solid oxygen carrier. Outlet streams include exhausted air (mostly N_2), and the combustion products (CO_2 and H_2O). Besides the inherent separation of CO_2 , another advantage of the CLC system is that nitrogen oxides are not produced.

Several practical implementations of this system have shown its feasibility. As described above, this configuration has been extended for simultaneous production of hydrogen.

3.1. Extended CLC configurations

Besides the conventional CLC, this work considers two alternative extended configurations involving three reactors: the exCLC and the CLC3 systems.

3.1.1. exCLC (Wolf and Yan, 2005)

In the exCLC configuration shown in Fig. 4, not only the CO_2 stream is inherently separated but also hydrogen is produced. The oxygen carrier (Ni or Fe in this work) circulates along with a carbon carrier (CaO) through three reactors. In the first reactor (air or oxidation reactor, OR), the oxygen carrier is oxidized with air; the

metal oxide is then fed to the remaining two reactors. Hydrogen production is achieved in a second reactor (fuel or reduction reactor, RR) by using an under-stoichiometric amount of metal oxide, so that the oxygen present is not sufficient for a complete oxidation of the fuel. In fact, partial oxidation and steam reforming take place at the same time in the RR reactor; the amount of active metal oxide controls the yield of produced hydrogen and carbon. Further, in order to separate the hydrogen from the CO_2 , the carbon carrier (calcium oxide, CaO) is used; the CO_2 will react with the CaO to produce calcium carbonate ($CaCO_3$). Then, CO_2 is removed from the gaseous phase. Finally, in the third reactor (Calcination Reactor, CR) the particles of calcium carbonate decompose into calcium oxide (carbon carrier) and CO_2 . The calcium carbonate decomposition is endothermic and, in order to maintain the required temperature, it is necessary to supply additional heat. Wolf and Yan (2005) suggest two alternatives. The first one is using the heat of a part of the flow of the hot particle stream leaving the air reactor; the second alternative is using hot steam obtained by cooling the hot metal oxide particles entering the fuel reactor. Global inlet streams include air, steam, fuel and both oxygen and carbon carriers. Outlet streams of the system are exhausted air (mainly nitrogen), a CO_2 rich stream and H_2 .

3.1.2. CLC3 (Chiesa et al., 2008)

The configuration known as the CLC3 system is depicted in Fig. 5. In the CLC3 configuration, the basic CLC arrangement is also modified by inserting a third reactor which produces H_2 . This configuration exploits an intermediate oxidation state of the circulating metal; for that reason, iron oxide (with multiple oxidation states) is recommended as the carrier. Commercial gas turbines can be adapted to operate in the specific conditions of the CLC3 arrangement which does not require additional novel technologies or high-risk components.

The CLC3 configuration includes two oxidation reactors (air and steam reactors, AR and SR) and one reduction reactor (fuel reactor, FR). Iron in its lower oxidation state (FeO) is further oxidized in the steam reactor to Fe_3O_4 . Iron oxidation is then completed in the air reactor to Fe_2O_3 . In the fuel reactor, the Fe_2O_3 is reduced back to FeO. Inlet streams are the fuel, air, steam and the circulating carrier. Outlet streams include exhausted air, a CO_2 rich stream and a H_2 rich stream.

Both, the exCLC and the CLC3 include an additional reactor and produce hydrogen. The exCLC can in theory use any oxygen carrier,

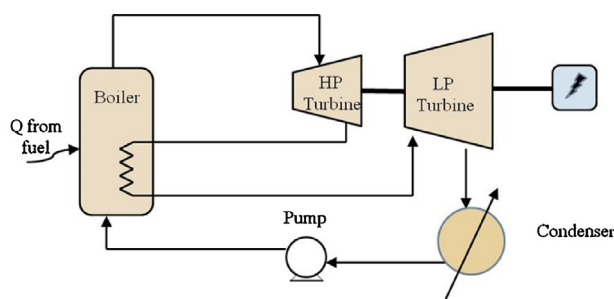


Fig. 6. Steam cycle.

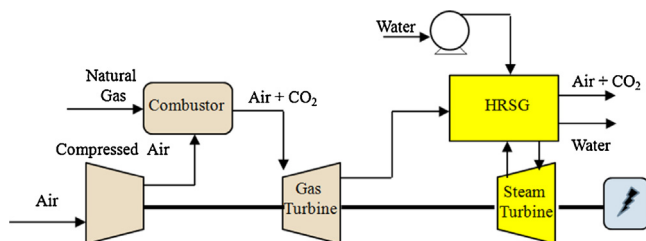


Fig. 7. Combined cycle.

but it also requires a carbon carrier. The CLC3 does not require a carbon carrier and, therefore, a less number of chemical reactions are involved, but an oxygen carrier with multiple oxidation states is needed.

3.2. Power generation plants

The three chemical looping combustion systems described above (CLC, exCLC and CLC3) have been incorporated into commercially available state-of-the-art power generation technologies. The power generation cycles used for the analysis include a combined cycle with steam injected gas turbines (STIG), a Humid Air Turbine cycle (HAT) and a simple steam cycle (SC).

3.2.1. Conventional steam cycle (SC) and combined cycle (CC)

Thermal power plants use water as working fluid. Energy from fuel gets transformed into electricity in a conventional steam cycle (SC, Fig. 6). Steam turbines are rotated with help of high pressure and high temperature steam and this rotation is transferred to a generator to produce electricity. External heat is added to the fluid in a reboiler in order to bring the fluid back to its original temperature; this completes the thermodynamic cycle. Pressure of the fluid remains the same, since it is free to expand in the heat exchanger tubes.

A combined-cycle power plant uses both a gas and a steam turbine to produce electricity from the same fuel than a traditional steam-cycle plant. The waste heat from the gas turbine is routed to the nearby steam turbine, which generates extra power. This configuration requires a heat recovery steam generator (HRSG) to capture exhaust heat from the gas turbine that would otherwise escape through the exhaust stack. The HRSG creates steam from the gas turbine exhaust heat and delivers it to the steam turbine. Most of the combined-cycle power plants use fossil fuel (natural gas) as external input of energy. That results in a natural gas combined cycle (NGCC) as the one shown in Fig. 7.

3.2.2. Steam injected gas turbine (STIG)

The STIG power plant of Fig. 8 is similar to the combined cycle; but there are two main differences between them. First, the STIG cycle does not involve a steam turbine. Second, high pressure vapor from the HRSG unit is injected into the combustion chamber at

a pressure higher than the combustion pressure to improve the efficiency of the gas turbine.

3.2.3. Humid air turbine cycle (HAT)

The HAT cycle (Fig. 9) is currently considered as the most advanced technology for the generation of electricity (Sullerey and Agarwal, 2008). The HAT cycle is an intercooled, regenerated cycle with a saturator (humidifier) that adds moisture to the air compressor discharge. The combustor inlet contains approximately 20% water vapor. The intercooling reduces the compressor work, while the water vapor in the exhaust gases increases the turbine output, so increasing the overall efficiency of the cycle. The configuration of the HAT cycle used in this work was taken from the work of Higuchi et al. (2003). After compression and intercooling, air comes in contact directly with hot water in the humidifier and it becomes humid air with 100% relative humidity. As a result, the flowrate of the working fluid increases, and the turbine generation power will also increase. The humid air flows into the combustion chamber after it is pre-heated by the turbine exhaust gas with the recuperator. The high temperature combustion gas is discharged, after the turbine is driven and the recuperator and economizer collect the exhaust heat. Both the intercooling exchangers and the economizer collect heat from the hot gases (air and turbine exhaust gases) and supply warm water. A part of the warm water evaporates by coming in contact directly with compressed air in the humidifier. Therefore, the temperature of the remaining warm water decreases; such water is then taken out of the bottom of the humidifier. Finally, that water exiting the humidifier is divided into two streams. A part of the flow is sent to the air coolers and the rest is sent to the economizer again; observe, that both of those separated streams serve the same purpose, as they are both used as a heat recovery medium by the high temperature gaseous streams (air in the case of the air coolers and exhaust gas in the case of the economizer). Such division, nevertheless, allows the control of the temperature levels of the water circulating within both the economizer and the humidifier. Typical values of temperature of the water entering and exiting the humidifier range between 135 °C (warm water at the top) and 70 °C (at the bottom).

4. Case-studies: integrating CLC and power generation technologies

This work considers 15 configurations, which integrate the CLC systems (CLC, exCLC, CLC3) and the power generation plants (SC, STIG, HAT) described on the previous section.

4.1. Oxygen carrier

Most of the technical literature on CLC has focused on the development of suitable oxygen carrier materials. Because of their favorable reductive/oxidative thermodynamic properties, metal oxides such as nickel, copper, cobalt, iron and manganese are good candidates. Iron and copper are two of the most common and cheapest metals available. On the other hand, nickel presents favorable thermodynamic properties. Then, among the various alternatives, supported nickel, iron and copper oxides have received the highest attention; however, CuO has the tendency to decompose at comparatively low temperatures (Arjmad et al., 2012; Garcia-Labiano et al., 2004; Adanez et al., 2006). In this work we have therefore selected nickel and iron as oxygen carriers for our simulation studies.

4.2. Configurations under investigation

Since we study iron and nickel as oxygen carriers, and given the three CLC systems and the three power cycles, 18 combinations

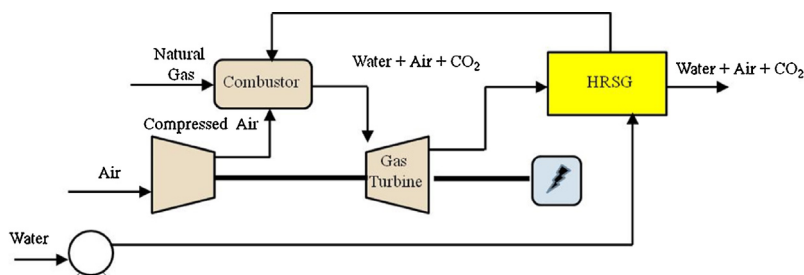


Fig. 8. STIG cycle.

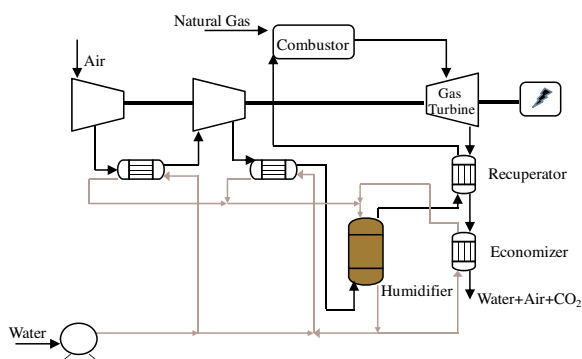


Fig. 9. HAT cycle.

Table 1
CLC based power generation plants under study.

Configuration	Chemical looping system	Carrier	Power cycle
1	Simple CLC	Ni	Steam cycle
2	Simple CLC	Ni	STIG
3	Simple CLC	Ni	HAT
4	Simple CLC	Fe	Steam cycle
5	Simple CLC	Fe	STIG
6	Simple CLC	Fe	HAT
7	exCLC	Ni	Steam cycle
8	exCLC	Ni	STIG
9	exCLC	Ni	HAT
10	exCLC	Fe	Steam cycle
11	exCLC	Fe	STIG
12	exCLC	Fe	HAT
13	CLC3	Fe	Steam cycle
14	CLC3	Fe	STIG
15	CLC3	Fe	HAT
16			NGCC

result. However, since the CLC3 configuration works only with a carrier with multiple oxidation states, three of the potential combinations were not feasible (nickel carrier and CLC3). For the purpose of comparison, a base case involving a NGCC was also analyzed. The 16 configurations studied are then summarized in Table 1.

Each of the configurations was modeled by using the AspenPlus process simulator v7.1. The simulation exercise involves 9 different sub-cases for each configuration. These sub-cases consider 3 levels of pressure for the CLC reactors (10, 20 and 30 bar) and three levels of turbine inlet temperature (TIT; 1050, 1020 and 1350 °C). Further, the optimization of the model parameters for each sub-case was achieved through a parametric study using the AspenPlus sensitivity analysis tool. Some of the main parameters analyzed include fuel flow, the air flow needed to achieve a specific TIT as well as the global power delivery of the plant.

As basic illustrations, Figs. 10, 11 and 12 show the Aspen models for the CLC system, the exCLC system and the CLC3 system, respectively. Temperature and pressure levels of each material stream are shown in those figures. As it has been described, the exCLC and the

CLC3 systems involve H₂ production, whereas the simple CLC system does not. Therefore, for the purposes of fair cost and energy efficiency comparisons, in the simulation of both the exCLC and the CLC3 systems, we included a fourth reactor. Such a fourth reactor is a hydrogen post combustor, where the hydrogen stream is consumed. In that way, the energy attained in the post combustor could be used to evaluate the net LHV energy efficiency of the system. Additional simulations details are given as follows.

4.2.1. Simulation of the CLC system

The simulation model of the simple CLC configuration includes two equilibrium reactors, an air compressor and a CO₂ turbine. The H₂O/CO₂ stream exiting the reduction reactor generates power in the CO₂ turbine. Then, a heat exchanger recovers thermal energy from the exhaust H₂O/CO₂ stream and water is separated; the resulting CO₂ stream is at this point ready for compression. The exhaust air stream at high temperature and pressure can later be sent to a turbine of a power generation cycle.

4.2.2. Simulation of the exCLC system

In order to achieve a practically pure CO₂ stream in the exCLC system, the calcination reactor is kept at 1 bar and 870 °C. Since the calcium carbonate decomposition is endothermic, additional energy has to be supplied to the calcinations reactor. A part of the energy provided in the hydrogen post combustor of the exCLC system was used for that purpose. Due to the purity of the CO₂ stream, a CO₂ turbine is not proposed (as in the simple CLC system); however, a heat exchanger recovers some of the energy of such stream to pre-heat the fuel fed to the system.

Further, the reduction reactor requires 750 °C for H₂ production, so that energy has to be removed from that reactor. As shown in Fig. 11, we achieve this result by exchanging heat with the air stream exiting the compressor.

4.2.3. Simulation of the CLC3 system

Similar to the CLC configuration, the model of the CLC3 system includes a CO₂ turbine and a heat exchanger used to separate CO₂ from water. Also, intercooling between two air compressors generates the steam required by the oxidation reactor.

4.2.4. Simulation of the steam cycle

Three pressure levels (three turbines) are used in our simulation of this power generation plant; high (1700 psi), intermediate (600 psi) and low (70 psi). Because of the three levels of pressure, the HRSG unit includes three economizers, three evaporators and five superheaters.

4.2.5. Simulation of the STIG cycle

The simulation model of the STIG cycle includes two main heat exchangers: an evaporator and a superheater. The evaporator generates steam by recovering some of the energy of the exhausted air/water stream exiting the system. The superheater increases the steam temperature by using energy from the exhaust gas exiting

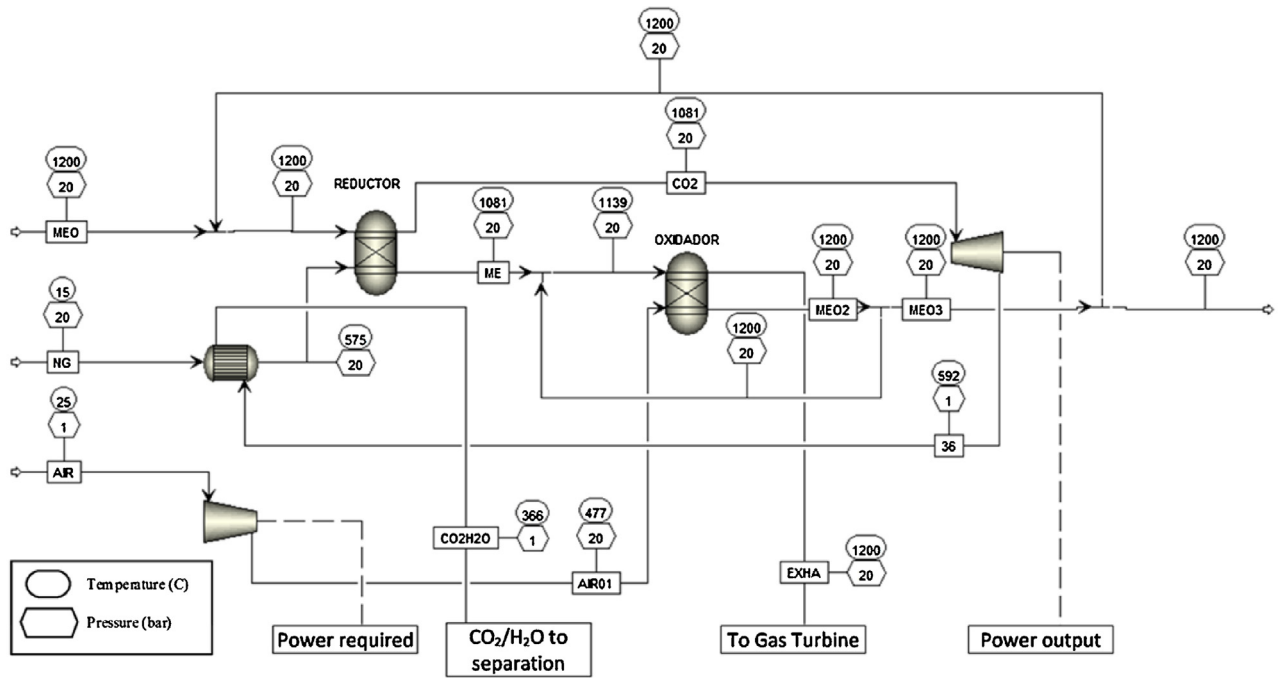


Fig. 10. AspenPlus model for a CLC system.

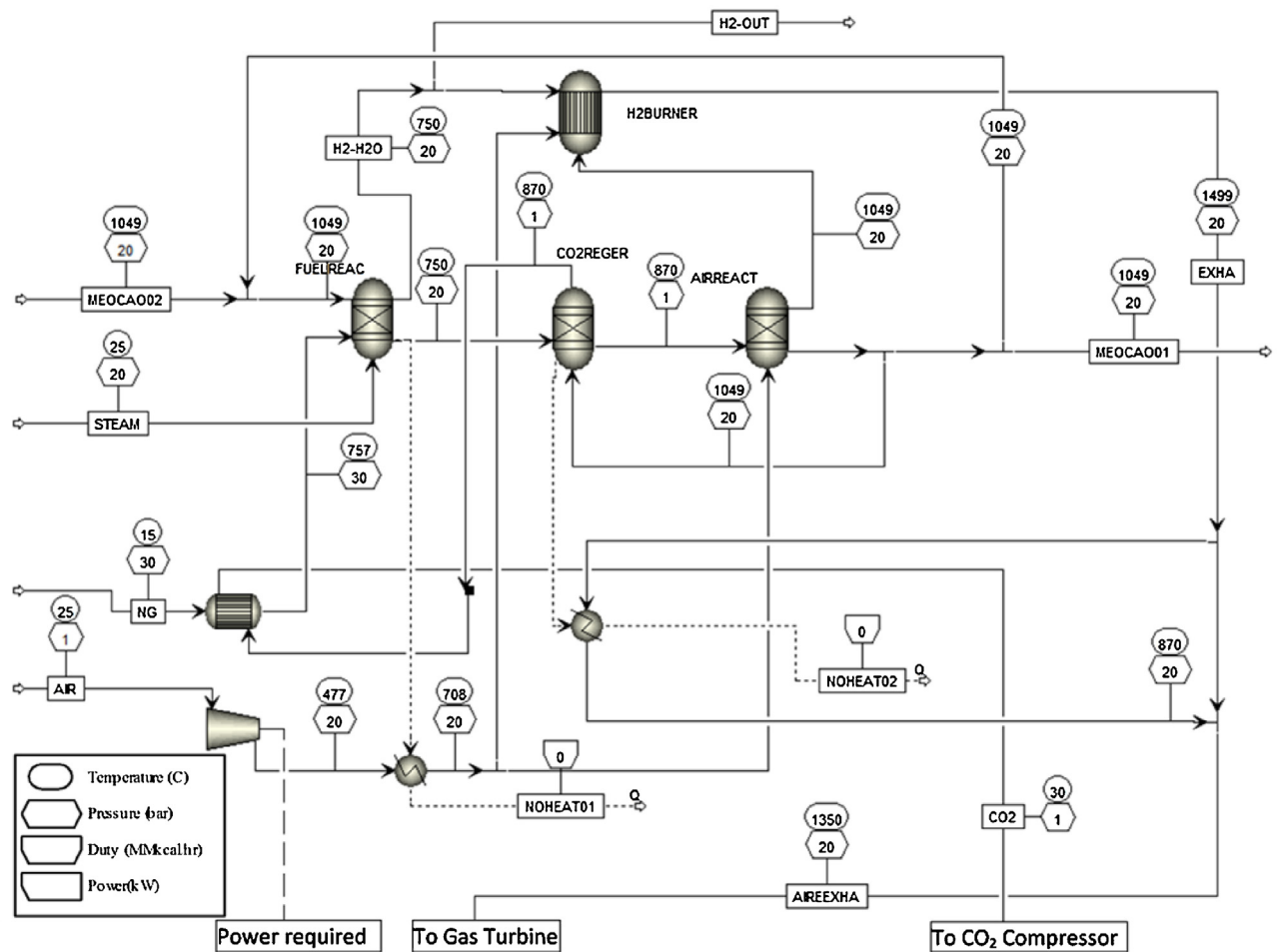


Fig. 11. AspenPlus model for the exCLC system.

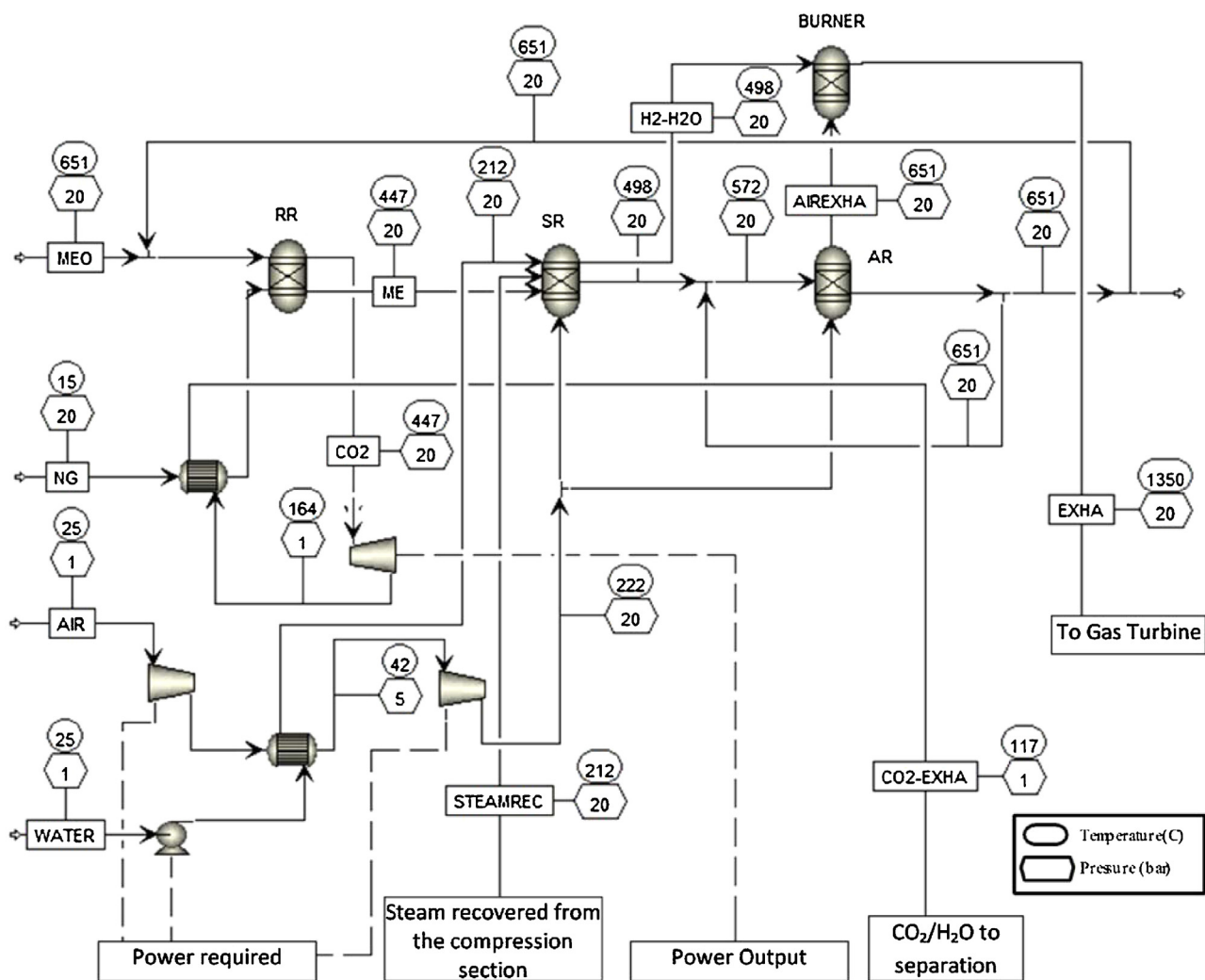


Fig. 12. AspenPlus model for a CLC3 system.

the gas turbine. The air compressor uses intercooling to reduce the energy required for compression and also to generate additional steam which is later superheated.

4.2.6. Simulation of the HAT cycle

In the model of the HAT cycle, two heat exchangers are used as the economizer and the recuperator. The humidifier is modeled as a physical equilibrium tray column without reboiler or condenser. As in the conventional configurations, air intercooling is used; the resulting warm water streams are sent back the humidifier. The cool water stream leaving the humidifier is then used for both the economizer and the air intercooling. Fig. 13 illustrates an AspenPlus model used for the simulation of the HAT cycle. As in the previous flowsheets, temperature and pressure levels of each material streams are shown in Fig. 13.

4.3. Fossil fuel: natural gas and its low heating value (LHV)

Natural gas, refinery gas and syngas have often been considered as fuels for CLC systems. Current technologies consider also coal-direct chemical looping configurations. This study considers the fuel described in Table 2. The net plant efficiency is estimated relative to the fuel LHV. Such a value is also shown in Table 2.

4.4. AspenPlus modeling and optimization

All of our simulation models use the Peng–Robinson Boston–Mathias (PR-BM) for fluid phases as well as the SOLIDS (for solid carriers) thermodynamic models provided in AspenPlus. As one of the main assumptions, all of the reactors consider chemical equilibrium and are modeled by the GIBBS model of the Aspen model library. The rest of the models and their main parameters are shown in Table 3. The same values are used in the simulations of all of the configurations.

During the model development, conventional combustor power plants and the various CLC systems were first simulated separately. Further integration and optimization of all of the outlet and inlet streams of both systems is then needed when substituting the conventional combustors by the CLC systems. To complete such a task, the AspenTech Design Specs tool was used to achieve specific operational conditions. For instance, given the fuel stream and the TIT, that tool allows the estimation of the air flow required. Similarly, the tool allows estimating the flows among the reactors on the exCLC to achieve adiabatic conditions on the oxidation reactor. As mentioned before, the AspenTech Sensibility Analysis tool was also used to achieve the optimal (highest) net LHV plant efficiency for each of the 9 instances of each configuration.

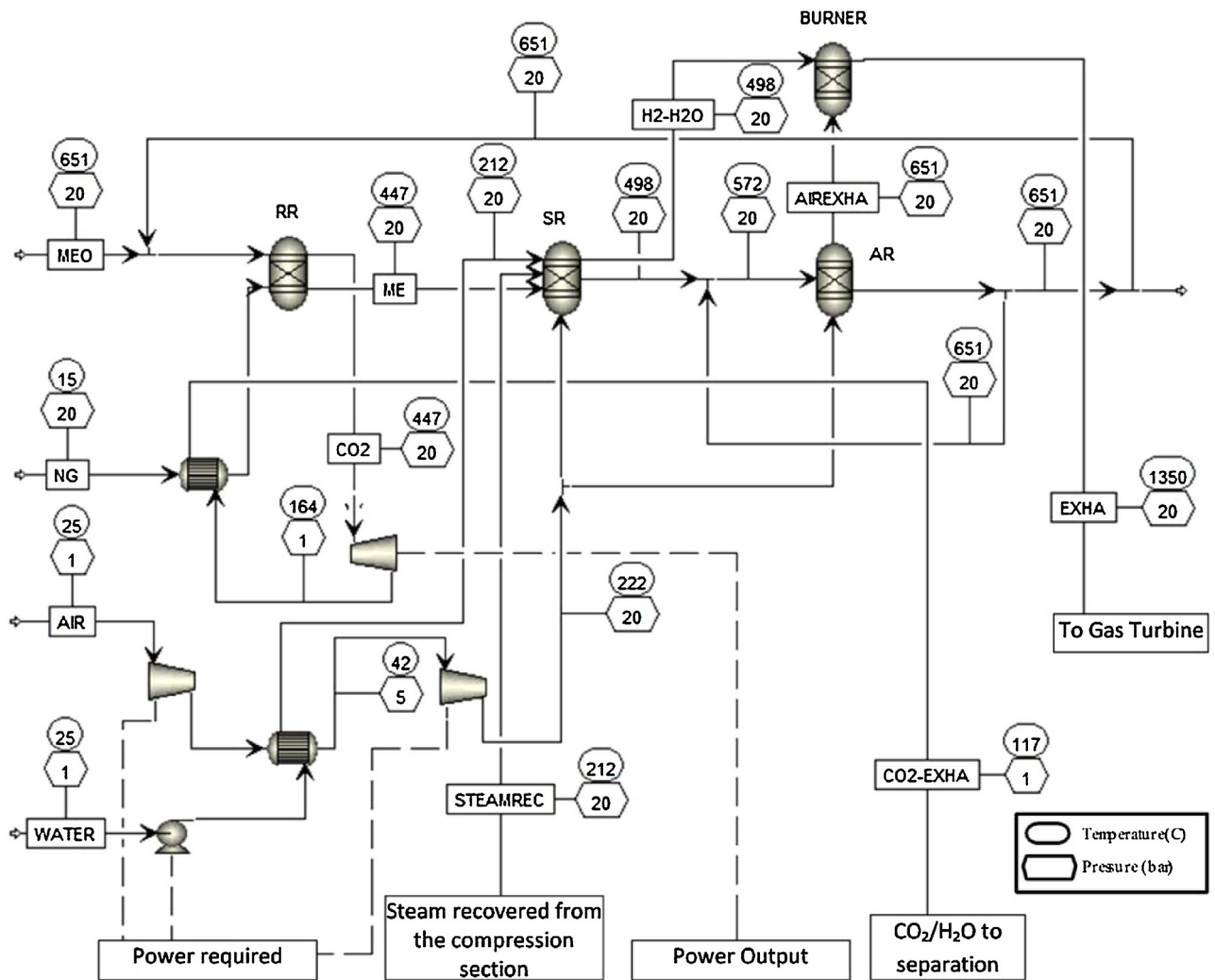


Fig. 13. AspenPlus model for the humid air turbine (HAT) cycle.

Table 2
Fuel composition and low heating value (LHV).

Component	Molar fraction	Molar flow (kmol/h)	Combustion enthalpy (kJ/mol)	Low heating value (MW)
Methane	0.8937	1622.07	-802.6	-361.63
Ethane	0.1011	183.50	-1428.6	-72.82
Propane	0.0052	9.44	-2043.1	-5.36
Total		1815.00		-439.80

Table 3
AspenPlus models and parameters.

Equipment	Aspen model	Parameters
Pumps	PUMP	Efficiencies: Isentropic 0.70
Compressors	COMPR	Efficiencies: Isentropic 0.85
Turbines	COMPR	Efficiencies: Isentropic 0.90
Heat exchangers	HEATX	Minimum approach: 10 °C
Heaters/coolers	HEATER	Minimum approach: 10 °C
Reactors	RGIBBS	Chemical equilibrium
Mixers/splitters	MIXER/FSPLIT	
Humidifier	RADFRAC	10 Equilibrium stages

4.5. Cost estimations

The Aspen Economic Evaluation tool, which is based on a Guthrie type of methodology, was used for the economic assessment of the power plant configurations. Table 4 shows the unit

cost of supported oxygen carriers. The values used for the cost of utilities correspond to information provided by the Mexican petroleum industry (4.7849 USD/MMBTU of fuel, 2.45 USD/m³ of process water and 0.0148 USD/m³ of cooling water). The chemical engineering cost plant index was used to update the cost

Maximum Net Plant Efficiencies

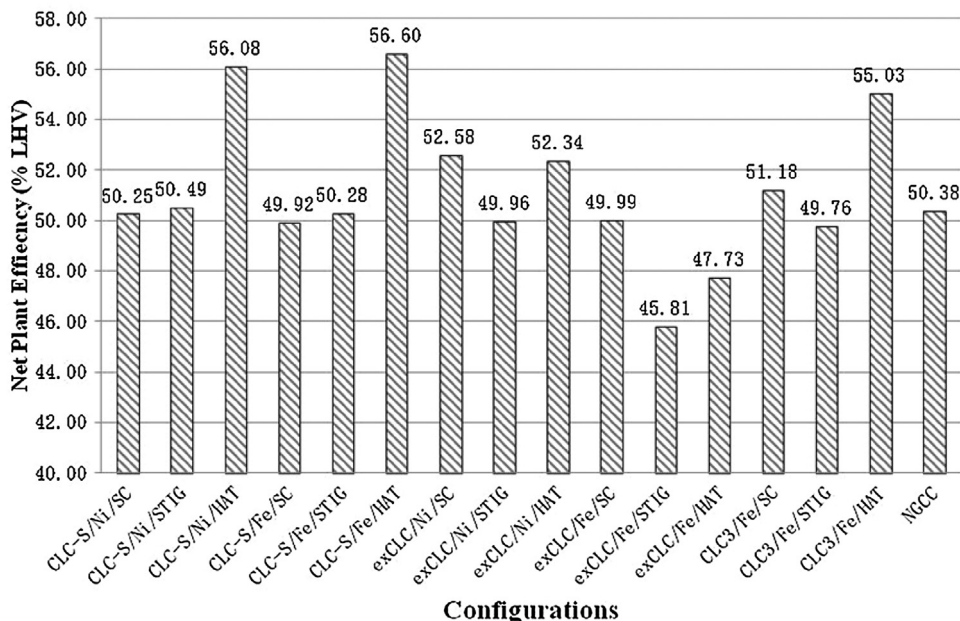


Fig. 14. Maximum net plant efficiencies for each configuration.

Table 4

Cost of supported oxygen carriers.

Configuration	Carrier/support	Composition (% mol)	Price (USD/kg)
CLC-Ni	NiO/alumina	0.25/0.75	24.14
CLC-Fe	Fe ₂ O ₃ /alumina	0.75/0.25	20.10
exCLC Ni	NiO/CaO/alumina	0.28/0.16/0.56	24.57
exCLC Fe	Fe ₂ O ₃ /CaO/alumina	0.36/0.10/0.54	20.18
CLC3	Fe ₂ O ₃ /alumina	0.60/0.40	20.19

estimation to the year of 2013. The estimation factors used for the calculation of the direct costs are the values recommended by the Aspen evaluation tool. 357 days of operation per year were assumed by considering 8 days per year for equipment maintenance. For the calculation of profit and revenue, a price for electricity of 409.87 USD/MWh was assumed.

5. Results and discussion

All of the calculations have been performed under the same basic assumptions and the same model parameters. Main results of our simulations include the values of net LHV plant efficiencies and the economic assessment of the various configurations. Seeking simplicity, many of the model specifications and results have been omitted, but all the information and models can be provided to the interested reader upon request.

5.1. Net LHV plant efficiencies

Table 5 shows the values for the net LHV plant efficiency of each of the CLC-power plant configurations. The value is the average of the 9 combinations resulting from the values of the reactors pressure and the TIT.

As per the individual simulations, the highest value obtained for the net efficiency is 56.60%, which corresponds to the simple CLC system into the HAT cycle with iron as carrier, and a reactor pressure of 10 bar and TIT of 1350 °C. Such a value is well above that obtained by the conventional NGCC. Fig. 14 shows the maximum efficiencies obtained for each of the 16 configurations. The lowest

Table 5

Average net LHV plant efficiency, η , for the configurations under investigation.

Configuration	Chemical looping system	Carrier	Power cycle	% η
1	CLC	Ni	Steam cycle	45.92
2	CLC	Ni	STIG	47.40
3	CLC	Ni	HAT	53.21
4	CLC	Fe	Steam cycle	47.45
5	CLC	Fe	STIG	48.08
6	CLC	Fe	HAT	53.80
7	exCLC	Ni	Steam cycle	50.29
8	exCLC	Ni	STIG	46.01
9	exCLC	Ni	HAT	51.28
10	exCLC	Fe	Steam cycle	46.54
11	exCLC	Fe	STIG	45.02
12	exCLC	Fe	HAT	45.53
13	CLC3	Fe	Steam cycle	48.87
14	CLC3	Fe	STIG	46.44
15	CLC3	Fe	HAT	52.76
16			NGCC	45.50

value is 45.81%, obtained by the exCLC system with iron as carrier integrated into the STIG cycle; the reactor pressure for that system is 30 bars and the TIT is 1140 °C.

In summary, the CLC-S/HAT combination resulted as the one with the highest potential in terms of thermal efficiency. It has been well documented that power generation with mass (water) injection result in higher turbine efficiencies because the working fluid of the turbine increases. In a STIG cycle, water is fed to a heat recovery steam generator that produces the steam injected to the combustion chamber of the gas turbine. The HAT cycle is more complex (see Sections 3.2.2 and 3.2.3 as well as Figs. 8, 9 and 13) due to the use of the air coolers, a humidifier and a recuperator. Recuperation is used to heat the humidified air and to provide the highest possible efficiency in the use of energy. Therefore, it is not surprising that configurations involving the HAT cycle present the highest thermal efficiency.

Regarding the effect of the oxygen carrier, as in most of the existing literature on this area, our simulations are limited in their scope. Issues such as stability, mechanical resistance, environmental

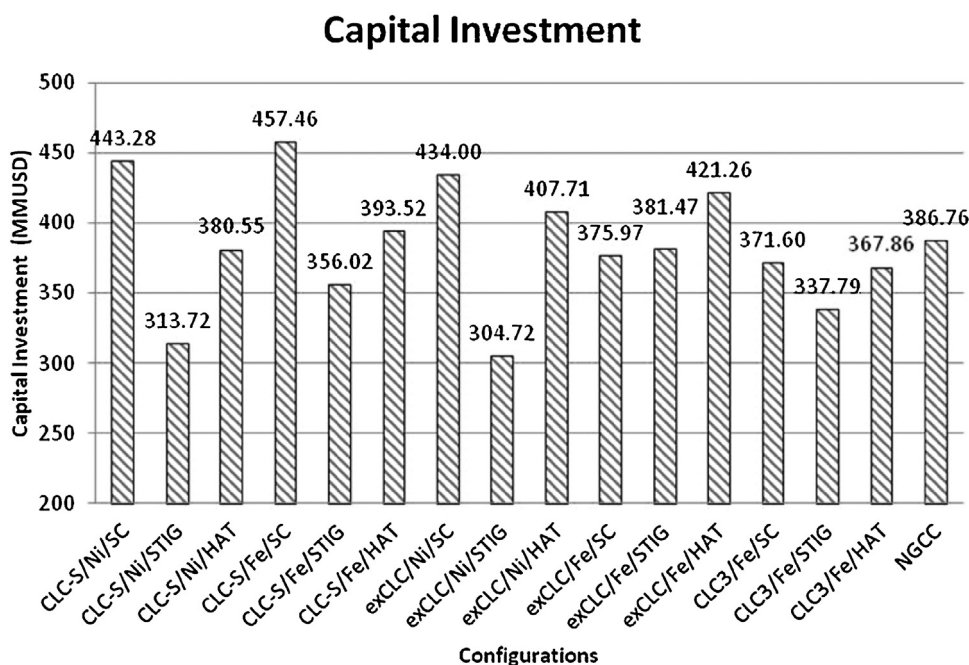


Fig. 15. Total capital investment for the maximum-efficiency CLC-based power plants.

Table 6

Operation cost, unit production cost and payback period for the CLC-based power generation plants.

Configuration	Operation cost (MMUSD/year)	Unit production cost (USD/MWh)	Payback period (years)
CLC-S/Ni/SC	176.87	93.41	3.02
CLC-S/Ni/STIG	145.23	76.32	1.97
CLC-S/Ni/HAT	172.88	81.82	2.45
CLC-S/Fe/SC	180.15	95.78	3.15
CLC-S/Fe/STIG	155.52	82.09	2.30
CLC-S/Fe/HAT	175.29	82.17	2.54
exCLC/Ni/SC	174.95	88.29	2.89
exCLC/Ni/STIG	143.82	76.38	1.92
exCLC/Ni/HAT	184.20	93.39	2.75
exCLC/Fe/SC	160.71	85.31	2.46
exCLC/Fe/STIG	163.22	94.53	2.60
exCLC/Fe/HAT	187.17	104.06	2.98
CLC3/Fe/SC	159.62	82.76	2.41
CLC3/Fe/STIG	151.74	80.92	2.17
CLC3/Fe/HAT	163.96	79.06	2.35
NGCC	162.62	85.66	2.54

Table 7

Average values of economic indicators for configurations involving the same CLC system.

CLC system	Average unit production cost (USD/MWh)	Average unit profit (USD/MWh)	Average payback period (years)
CLC-S	82.17	152.23	2.57
exCLC	90.33	149.41	2.98
CLC3	80.92	155.30	2.31

impact, etc., are not studied and our analysis. Our results may only show the carrier reactivity and their effect on the reactions yields. However, chemical equilibrium was also assumed for all of the reactors and configurations. We can then argue that the chemical equilibrium reactivity of iron favors the higher efficiency value of the configuration CLC-S/Fe/HAT when compared to the similar configuration that uses nickel.

5.2. Costs

Results from the economic evaluation are shown in Fig. 15 and Tables 6 and 7. The values correspond to the configurations with maximum plant efficiencies already shown in Fig. 14. By comparing

common CLC/oxygen carrier combinations using the three power plant cycles, Fig. 15 shows that, regardless of the net plant efficiency, SC (steam cycle) power plants involve the highest capital investment values; the HAT cycle presents intermediate values and the STIG cycle displays the lowest values. For processes that include the complexity and combined effects of the CLC systems and the state-of-the-art power generation cycles, it is difficult to establish a particular parameter or condition which is the critical one (or more significant) with respect to the capital investment of the whole system. Nevertheless, our study has shown that the capital cost of compressors and turbines represents the highest percentage of the capital costs of a power plant. Our configuration for the Steam Cycle (SC) includes three turbines (high, low and intermediate

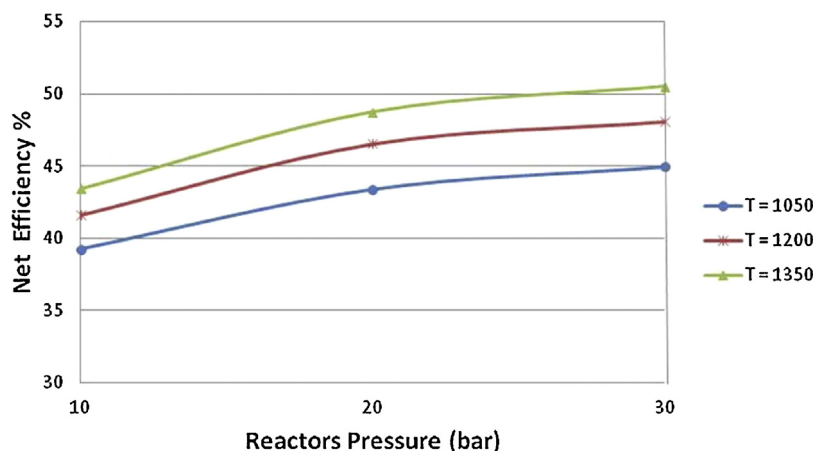


Fig. 16. Effect of TIT on the net plant efficiency for configuration 2 (CLC/Ni/STIG).

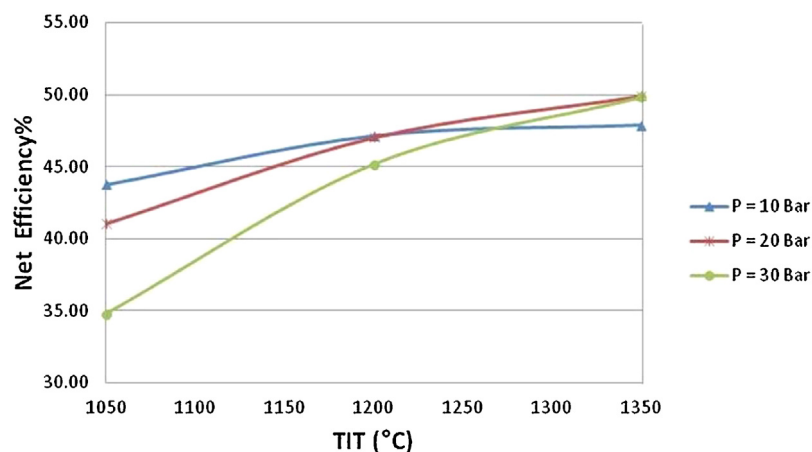


Fig. 17. Effect of pressure on the net plant efficiency for configuration 4.

pressure turbines); therefore, power plants including the SC cycle are expected to present the highest capital investment values. On the other hand, both the STIG and the HAT cycles include only one gas turbine and involve the injection of water to the air supplied to the turbine; however, as explained in the previous subsection, the HAT cycle is more complex. As a direct consequence, this complexity, in terms of the pieces of equipment required, results in a higher capital investment for the HAT cycle than that needed by the STIG cycle.

Table 6 presents the present total annual operation cost, the unit production cost and the payback period of the 16 configurations studied in this work. Payback period calculations were performed by using the cost of domestic electricity in Mexico in April, 2014 (US\$409.87/MWh). The current average cost of electricity in the US is about one half of such value, so that the payback period would change by a factor of 2 in that case.

Table 7 is intended to compare the performance of the CLC systems in the various combinations of oxygen carrier/power plant. Values of Table 7 represent average values of all of the configurations involving the same CLC system. Interestingly, configurations involving the CLC3 system present the best performance on each of the individual indicators. On the contrary, the exCLC system shows the poorest performance; finally, the CLC-S system displays intermediate results.

5.3. Effect of TIT and pressure

Our results agree with and confirm the results reported in the literature on this regard. In general, the higher the TIT, the

higher the net plant efficiency. Fig. 16 depicts the behavior for the CLC/Ni/STIG configuration, whose results are typical for this analysis. The behavior with respect to the reactors pressure, however, does not present a general trend, as it is shown in Fig. 17 for configuration 4 (CLC/Fe/SC).

6. Summary and conclusions

This work complements the existing literature by providing a comparative study among different power plant cycles including chemical looping combustion systems. The study of configurations including the CLC3 system with the STIG and HAT cycles are of particular value. The decisions about the carrier, power cycles and CLC systems intend to consider configurations with state-of-the-art commercially available components. Results confirm the potential of CLC systems for its integration to power generation cycles. The simulations also reveal the many operational complications and assumptions that need to be considered, analyzed and validated in practical implementations of the configurations studied. Under the same basis for comparison, net LHV plant efficiencies obtained in CLC-base power generation plants are superior or competitive to currently used technologies with the advantage of its potential for CO₂ capture. Unit production costs of energy in CLC based power plants are also comparable to current commercially available technologies. Although we understand the limitations of our approach for cost estimations, the calculations in all of the configurations were performed under the same basis and assumptions, so that they are still useful for comparison purposes.

The CLC-S/HAT combination resulted as the one with the highest potential in terms of thermal efficiency. However, configurations involving the CLC3 system present the best performance on each of three economic individual indicators (unit production costs, profit and payback period); the exCLC system shows the poorest performance whereas the CLC-S system displays intermediate results.

Acknowledgements

The authors acknowledge the financial support provided by CONACYT (National Mexican Council for Science and Technology, Grant 104672), DGEST (4528.12-P) (Technical Undergraduate Education Directorate, Mexico) and the Vishwamitra Research Institute.

References

- Adanez J, Garcia-Labiano F, de Diego LE, Gayan P, Celaya J, Abad A. Nickel-copper oxygen carriers to reach zero CO and H₂ emissions in chemical-looping combustion. *Ind Eng Chem Res* 2006;45:2617–25.
- Adanez J, Abad A, Perez-Vega R, de Diego LE, Garcia-Labiano F, Gayan P. Design and operation of a coal-fired 50 kWh chemical looping combustor. *Energy Proc* 2014;63:63–72.
- Arjmad M, Azad AM, Leion H, Mattisson T, Lyngfelt A. Evaluation of CuAl₂O₄ as an oxygen carrier in chemical-looping combustion. *Ind Eng Chem Res* 2012;51:13924–34.
- Brandvoll O, Bolland O. Inherent CO₂ capture using chemical looping combustion in a natural gas fired power cycle. *J Eng Gas Turbines Power* 2004;126:316–21.
- Chiesa P, Lozza G, Malandrino A, Romano M, Piccolo V. Three-reactors chemical looping process for hydrogen production. *Int J Hydrogen Energy* 2008;33(9):2233–45.
- Connell DP, Lewandowski DA, Ramkumar S, Phalak N, Statnick RM, Fan LS. Process simulation and economic analysis of the Calcium Looping Process (CLP) for hydrogen and electricity production from coal and natural gas. *Fuel* 2013;105:383–96.
- Consonni S, Lozza G, Pelliccia G, Rossini S, Saviano F. Chemical-looping combustion for combined cycles with CO₂ capture. *J Eng Gas Turbines Power* 2006;128:525–34.
- Fan J, Zhu L. Performance analysis of a feasible technology for power and high-purity hydrogen production driven by methane fuel. *Appl Therm Eng* 2015;75:103–14.
- Garcia-Labiano F, de Diego LF, Adanez J, Abad A, Gayan P. Reduction and oxidation kinetics of a copper-based oxygen carrier prepared by impregnation for chemical-looping combustion. *Ind Eng Chem Res* 2004;43:8168–77.
- Gupta P, Velazquez-Vargas LG, Li F, Fan LS. Chemical looping reforming process for the production of hydrogen from coal. In: Proceedings of the 23rd annual international Pittsburgh coal conference; 2006.
- Higuchi S, Hatamiya S, Seiki N, Marushima S. A study of performance of advanced humid air turbine systems. In: The proceedings of the international gas turbine congress; 2003.
- Ishida M, Jin H. A novel chemical-looping combustor without NO_x formation. *Ind Eng Chem Res* 1996;35:2469–72.
- Ishida M, Jin H. CO₂ recovery in a power plant with chemical looping combustion. *Energy Convers Manage* 1997;38:5187–92.
- Ishida M, Jin H. Fundamental study on a novel gas turbine cycle. *Trans ASME* 2001;123:10–4.
- Jin H, Ishida M. A novel gas turbine cycle with hydrogen-fueled chemical looping combustion. *Int J Hydrogen Energy* 2000;25:1209–15.
- Jin H, Ishida M. A new type of coal gas fueled chemical-looping combustion. *Fuel* 2004;83:2411–7.
- Jordal K, Gunnarsson J. Process configuration options for handling incomplete fuel conversion in CO₂ capture: case study on natural gas-fired CLC. *Int J Greenh Gas Control* 2011;5:805–15.
- Kim HR, Wang D, Zeng L, Bayham S, Tong A, Chung E, et al. Coal direct chemical looping combustion process: design and operation of a 25-kW(th) sub-pilot unit. *Fuel* 2013;108:370–84.
- Olaleye AK, Wang M. Techno-economic analysis of chemical looping combustion with humid air turbine power cycle. *Fuel* 2014;124:221–31.
- Ryden M, Lyngfelt A, Mattisson T. Synthesis gas generation by chemical-looping reforming in a continuously operating laboratory reactor. *Fuel* 2006;85:1631–41.
- Sullerey RK, Agarwal A. Performance improvement of gas turbine cycles. *Int J Turbo Jet-Engines* 2008;25:209–19.
- USEPA. 2013 US Greenhouse Gas Emissions Data. Inventory of U.S. Greenhouse Gas Emissions and Sinks 1990–2013. US Environmental Protection Agency; 2015.
- Wolf J, Yan J. Parametric study of chemical looping combustion for tri-generation of hydrogen, heat, and electrical power with CO₂ capture. *Int J Energy Res* 2005;29:739–53.
- Zhu L, Fan J. Thermodynamic analysis of H₂ production from CaO sorption-enhanced methane steam reforming thermally coupled with chemical looping combustion as a novel technology. *Int J Energy Res* 2015;39:356–69.
- Zhu L, Jiang P, Fan J. Comparison of carbon capture IGCC with chemical-looping combustion and with calcium-looping process driven by coal for power generation. *Chem Eng Res Des* 2015;104:110–24.