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EVALUATION OF IRON AND NICKEL-BASED OXYGEN CARRIERS FOR NATURAL GAS CHEMICAL LOOPING COMBUSTION SYSTEMS

IULIA-MARIA BODEA[a], CALIN-CRISTIAN CORMOS[a]

ABSTRACT. Chemical looping combustion (CLC) is a innovative technology used to capture CO_2, in which a solid oxygen carrier is circulated between two interconnected bed reactors. A fuel gas is oxidized to carbon dioxide and water by the oxygen carrier. The reduced oxygen carrier is transported to the air reactor where it is oxidized back to its original state by air. This paper investigates two natural gas CLC processes using ferric oxide and nickel oxide as oxygen carriers. The oxygen carriers are reduced in the temperature range 750-850°C while the oxidation temperature is between 850-950°C. The processes studied have the net electrical efficiencies in the range of 41-42% and the CO_2 capture rate is about 99%.

Keywords: *Chemical looping combustion (CLC), Power generation, Oxygen carriers, Carbon Capture and Storage (CCS)*

INTRODUCTION

The effect of carbon dioxide emissions for exacerbating the greenhouse effect is well known [1]. Carbon dioxide emissions derived from human activities have increased the concentration of greenhouse gases in the atmosphere, contributing to global climate change and increasing global temperature [2]. About a third of the global CO_2 emissions comes from the burning of fossil fuels in power generation sector [1].

Chemical Looping Combustion (CLC) is one promising techniques used to combine fuel combustion and pure CO_2 production in situ allowing for CO_2 sequestration [3]. This technology was first proposed primarily for the combustion of gaseous fuels and only recently been considered for solid fuels such as coal without gasification of the coal first to syngas [4]. CLC is a two-step gas combustion process that produces a pure CO_2 stream, ready for compression and sequestration [5]. The process is composed of two fluidized bed reactors, an air reactor and a fuel reactor, as shown in Figure 1. The fuel is introduced to the fuel reactor where it reacts with an oxygen carrier to CO_2

[a] "Babeş-Bolyai" University of Cluj-Napoca, Faculty of Chemistry and Chemical Engineering, Arany Janos Street 11, 400028 Cluj-Napoca, Romania; Emails: iulyya_b@yahoo.com, cormos@chem.ubbcluj.ro

and H_2O. The reduced oxygen carrier is transported to the air reactor where it is oxidized back to its original state by air. As a result, CO_2 can be inherently separated in this combustion process. The total amount of heat released in the air and the fuel reactor is equal to the heat released from normal combustion thus separating CO_2 without any losses in energy [6-7].

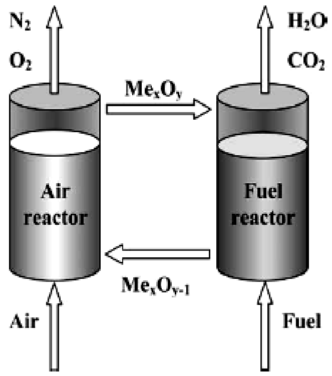

Figure 1. Chemical looping combustion (CLC)

In the fuel reactor, the metal oxide is reduced by the following general chemical reaction for a hydrocarbonated fuel (like natural gas or other hydrocarbons) [1]. The same reactions can take place also in case of syngas resulted from gasification of catalytic reforming processes.

$$(2n+m)\ Me_xO_y + C_nH_{2m} \rightarrow (2n+m)\ Me_xO_{y-1} + n\ CO_2 + m\ H_2O \qquad (1)$$

Me_xO_y is a metal oxide and Me_xO_{y-1} represents its reduced form.

The particles of oxygen carrier are transferred to the air reactor where they are regenerated by taking up oxygen from the air.

$$Me_xO_{y-1} + \frac{1}{2} O_2 \rightarrow Me_xO_y \qquad (2)$$

The oxidized oxygen-carrier is transported back to the fuel reactor and is reduced again. The reduction of the oxygen-carrier (1) can be either endothermic or exothermic, depending on the metal oxide and the fuel, while the oxidation (2) is exothermic [1-2]. Ideally, the number of reduction–oxidation cycles of the oxygen carrier (OC) would be infinite. However, the OC material must be renewed as a consequence of particle attrition/fragmentation or reactivity loss during the reduction/oxidation cycles and a makeup flow of new material is necessary.

The properties of the oxygen carrier are vital for the practice of the process of CLC. Metal oxides with their reduced oxides or metals should have a strong affinity for reaction with gaseous fuel as well as a high rate of oxidation by air [3]. Metal oxides of Fe, Ni, Co, Cu, Mn, and Cd have been discussed in the literature for CLC of gaseous fuels such as natural gas and CH_4 [4]. Iron oxide is cheaper than other metal oxides [1] but Ni-based oxygen carriers have been the most extensively materials analysed in the literature because they have very high reactivity and good performance working at high temperatures [5]. Beside of promising energy efficiencies, the chemical looping systems are also reducing significantly the emissions of nitrogen oxides resulted from fuel conversion. The main responsible for this fact is the decoupling the air environment (air reactor) from fuel (fuel reactor). Also, the high temperature heat recovery of chemical systems is implying higher pressure and temperature of the generated steam which means more power generated in the steam turbine.

RESULTS AND DISCUSSION

This paper describes two processes of the carbon dioxide capture using a natural gas-based chemical looping combustion system. The processes are identical in design, the difference is in terms of substance used as oxygen carrier. The oxygen carriers used are ferric oxide (Fe_2O_3) and nickel oxide (NiO). The process is composed of two interconnected fludized bed reactors [6,8] as shown in Figure 2.

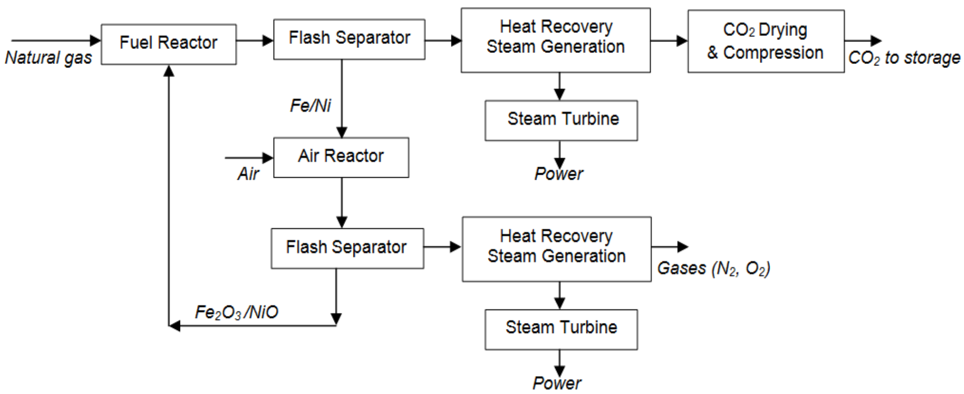

Figure 2. Chemical looping combustion for power generation

The natural gas having 30°C and 15 bar comes in contact with the oxygen carrier in the fuel reactor. The reduction of the oxygen carrier takes place at about 750-850°C and 15 bar, according to the chemical reactions (3) and (4) [8-9]:

$$4Fe_2O_{3(s)} + 3CH_{4\,(g)} \rightarrow 8Fe_{(s)} + 3CO_{2(g)} + 6H_2O_{(g)} \quad (3)$$

$$4NiO_{(s)} + CH_{4(g)} \rightarrow 4Ni_{(s)} + CO_{2(g)} + 2H_2O_{(g)} \quad (4)$$

The stream which leaves the reactor is sent to a flash separator where the solid phase is separated from the gas phase. The rich CO_2 stream leaves the flash to the top and is sent to a heat recovery steam generation. The CO_2 hot stream is then cooled down with cooling water, at around 40°C, the temperature is achieved by using a series of heat exchangers (heat recovery steam generator - HRSG). The steam obtained in heat recovery steam generators by cooling the hot streams reaches a steam turbine where heat is converted into electricity. The exhausted steam leaves the turbine, then it is condensed and recycled back in the cycle (steam – Rankine cycle).

The CO_2 cooled stream is sent to a compression unit, which has 3 compression stages with intercoolers. In the first stage the gas is compressed from 14 bar to 20 bar. The stream is cooled at 40°C and enters in a flash separator, used to remove the water from the process. Cooling and separation are made after each stage of compression. In the second stage the pressure is increased from 20 bar to 70 bar, then the pressure reaches in the third stage 120 bar. The compression stages were used instead of one compressor because one compressor needs more energy to achieve 120 bar than 3 compression stages. Another argument is to avoid the overheating of the compressors.

The solid stream coming from the bottom of the flash separator is sent to the air reactor where is oxidized with air at 850-950°C, according to the reactions (5) and (6).

$$4Fe_{(s)} + 3O_{2\,(g)} \rightarrow 2Fe_2O_{3(s)} \quad (5)$$

$$4Ni_{(s)} + 2O_{2(g)} \rightarrow 4NiO_{(s)} \quad (6)$$

The oxygen carrier obtained (ferric oxide/nickel oxide) is recycled to the reduction reactor. The gas stream leaves the flash separator to the top and is sent, like the CO_2 stream, to a integrated combined cycle. Nitrogen makes up the main part of air but is inert in the reaction equation (5) and (6). Therefore, the gas phase leaving the air reactor consist of nitrogen and excess oxygen [10-11].

The natural gas composition and the equipments main design assumptions used in the mathematical modeling and simulation are presented in Table 1. ChemCAD was used as simulation software.

The material balances for the two processes are given in Tables 2 and 3. The inlet and outlet mass flow represents the mass flow of the components entering and leaving the reactors. Table 2 and 3 shows that the natural gas is fully oxidized to CO_2 and water. The conversion of ferric oxide to iron is about 98.6 % in the fuel reactor while the oxidation of iron to ferric oxide is complete in the air reactor (Table 2). Regarding the process using nickel oxide as oxygen carrier, in the fuel reactor the reduction of nickel oxide to nickel is 100 % and the oxidation of nickel to nickel oxide is also complete (Table 3). These results are in line with experimental data reported in the literature [2-3].

Table 1. Main design assumptions

	Parameters	Fe_2O_3/Fe	NiO/Ni
Natural gas	Temperature (°C)	30.00	
	Pressure (bar)	15.00	
	Gas composition (% vol.)		
	Methane	89.00	
	Nitrogen	0.89	
	Carbon dioxide	2.00	
	Ethane	7.00	
	Propane	1.00	
	I-Butane	0.05	
	N-Butane	0.05	
	I-Pentane	0.005	
	N-Pentane	0.004	
	Hexane	0.001	
	Hydrogen Sulfide	0.00001	
	Calorific value (MJ/kg dry)		
	Gross (HHV)	51.473	
	Net (LHV)	46.502	
Fuel reactor	Reactor type	Gibbs	Gibbs
	Temperature (°C)	750.00-850.00	750.00-850.00
	Pressure (bar)	15.00	15.00
	Pressure drop (bar)	1	1
Air reactor	Temperature (°C)	850.00-950.00	850.00-950.00
	Pressure (bar)	14.00	14.00
	Fractional conversion	>99%	>99%
Heat exchangers	Minimum temperature difference (°C)	10.00	10.00
Expander	Expander efficiency (%)	65.00	65.00
CO_2 compression	Delivery pressure (bar)	120.00	120.00
	Compressor efficiency (%)	85.00	85.00
	Number of compression stages	3	3

Table 2. Material balance for CLC using ferric oxide as oxygen carrier

Parameters	Fuel reactor		Air reactor	
	Inlet	Outlet	Inlet	Outlet
Pressure (bar)	15.00	14.00	14.00	14.00
Temperature (°C)	799.68	850.00	267.56	949.74
Total mass flow (t/h)	655.68	655.68	3057.37	3057.37
Solid mass flow (t/h)	606.83	426.18	426.18	606.83
Gas mass flow (t/h)	48.85	229.48	2631.19	2450.56
Solid phase composition (% wt.)				
Ferric oxide	100.00	1.37	1.37	100.00
Iron	0.00	98.63	98.63	0.00

Parameters	Fuel reactor		Air reactor	
	Inlet	Outlet	Inlet	Outlet
Gas phase composition (% vol.)				
Carbon dioxide	2.00	34.66	0.03	0.03
Methane	89.00	0.00	0.00	0.00
Oxygen	0.00	0.00	20.73	15.50
Nitrogen	0.89	0.28	77.29	82.39
Water	0.00	65.05	1.03	1.09
Hydrogen sulfide	0.00001	0.00	0.00	0.00
Argon	0.00	0.00	0.90	0.90
Ethane	7.00	0.00	0.00	0.00
Propane	1.00	0.00	0.00	0.00
N-Butane	0.05	0.00	0.00	0.00
N-Pentane	0.004	0.00	0.00	0.00
N-Hexane	0.001	0.00	0.00	0.00
I-Butane	0.05	0.00	0.00	0.00
I-Pentane	0.005	0.00	0.00	0.00

Table 3. Material balance for CLC using nickel oxide as oxygen carrier

Parameters	Fuel reactor		Air reactor	
	Inlet	Outlet	Inlet	Outlet
Pressure (bar)	15.00	14.00	14.00	14.00
Temperature (°C)	727.00	850.00	216.98	950.29
Total mass flow (t/h)	892.21	892.21	3292.48	3292.48
Solid mass flow (t/h)	843.36	662.73	662.73	843.36
Gas mass flow (t/h)	48.85	229.48	2629.75	2449.12
Solid phase composition (% wt.)				
Nickel oxide	100.00	0.00	0.00	100.00
Nickel	0.00	100.00	100.00	0.00
Gas phase composition (% vol.)				
Carbon dioxide	2.00	34.66	0.03	0.03
Methane	89.00	0.00	0.00	0.00
Oxygen	0.00	0.00	20.73	15.50
Nitrogen	0.89	0.28	77.29	82.39
Water	0.00	65.05	1.03	1.09
Hydrogen sulfide	0.00001	0.00	0.00	0.00
Argon	0.00	0.00	0.90	0.90
Ethane	7.00	0.00	0.00	0.00
Propane	1.00	0.00	0.00	0.00
N-Butane	0.05	0.00	0.00	0.00
N-Pentane	0.004	0.00	0.00	0.00
N-Hexane	0.001	0.00	0.00	0.00
I-Butane	0.05	0.00	0.00	0.00
I-Pentane	0.005	0.00	0.00	0.00

Table 4 presents the composition of the carbon dioxide stream for the 2 cases studied versus the proposed specification [12]. The proposed specification is considering the requirement of transport and storage options (Enhanced Oil Recovery – EOR storage option was considered being the most restrictive case). For both processes studied the CO_2 content is bigger than the proposed limit (95 % vol.).

Table 4. Quality specification of captured carbon dioxide stream

Composition (% vol.)	Proposed specification	Fe_2O_3/Fe	NiO/Ni
CO_2	>95.00	98.82	98.82
CO	<2000 ppm	0.00	0.00
N_2	<4.00	0.81	0.81
O_2		0.00	0.00
Ar		0.00	0.00
H_2		0.00	0.00
H_2S	<100 ppm	9 ppm	9 ppm
H_2O	<250 ppm	0.36	0.36

Table 5 presents the main plant performance indicators for the 2 evaluated cases. The methane input is 500 MW_{th} and it is expressed taking into consideration the lower heating value (LHV). The overall efficiency of the plant was calculated considering the difference between power generated and power consumed (net power output), divided by the fuel (natural gas) input.

Table 5. Overall plant performance indicators

Main plant data	Units	Fe_2O_3/Fe	NiO/Ni
Methane input (C=A*B/3600)	MW_{th}	500.00	500.00
Methane flow rate (A)	t/h	38.708	38.708
Natural gas LHV (B)	MJ/kg	46.502	46.502
Power generated (D)	MW_e	456.01	456.05
Steam turbine	MW_e	164.13	164.21
Purge gas expander	MW_e	291.87	291.84
Power consumed (E)	MW_e	247.11	246.49
Air compressors	MW_e	239.77	239.64
CO_2 compressors	MW_e	5.10	5.10
Process pumps	MW_e	1.28	1.28
Cooling water pumps	MW_e	0.94	0.45
CO_2 capture rate	%	99.07	99.07
Plant efficiency ((D-E)/C*100)	%	41.77	41.91

The results show that the processes studied have the gross efficiency in the range of 44-45 % and the net efficiency in the range of 41-42 %. Regarding the rate of carbon dioxide capture the two processes have the same capture rate, about 99%. To calculate the CO_2 capture rate was taken into consideration the amount of CO_2 in the water output stream and gas output stream. These results underline an important advantage of chemical looping systems namelly high efficiency in condition of a total decarbonisation of the fuel used. In term of the two evaluated metalic oxides, there is no significant difference between them in term of technical performances [13-14]. However, ferric oxide could be the most preferable choice considering the wide distribution and the potential integration of spent oxide into metalurgy sector.

The carefully heat and power integration is a fundamental pre-condition of the carbon capture technologies to reduce the ancillary energy consumptions. In this study, in order to evaluate the possibilities of integration of the chemical looping CO_2 capture process, a pinch analysis was performed. In the power cycle the hot streams are cooled with cooling water. A heat-integration problem involves transferring heat from hot streams to cold streams so that each stream reaches its desired target temperature while minimizing the utility consumptions (including heating and cooling utilities) [15-18].

The composite curves (Figures 3 and 5) represent the hot and cold streams on a single diagram and determine the minimum utility duties for the entire system. Horizontal lines represent constant-temperature utilities. For condensing and vaporizing streams as hot and cold streams, respectively, a 1°C temperature change was considered [15].

The grand composite curve (Figures 4 and 6) displays the net heat-flow characteristics of a process versus its temperature and provides the same overall energy target as the composite curves.

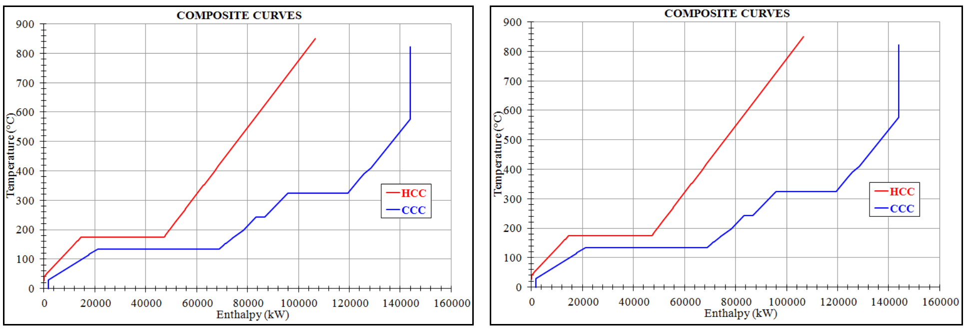

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Figure 3. Composite curves for heat recovery from CO_2 stream (fuel reactor)
a. CLC using ferric oxide; b. CLC using nickel oxide

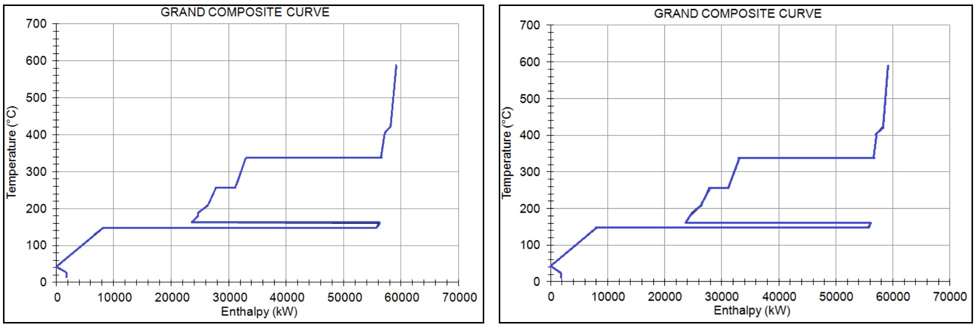

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Figure 4. Grand composite curve for heat recovery from CO_2 stream (fuel reactor) a. CLC using ferric oxide; b. CLC using nickel oxide

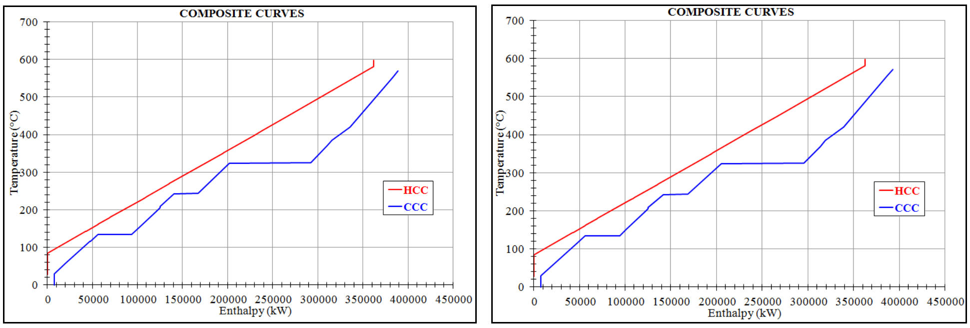

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Figure 5. Composite curves for heat recovery from spent air stream (air reactor) a. CLC using ferric oxide; b. CLC using nickel oxide

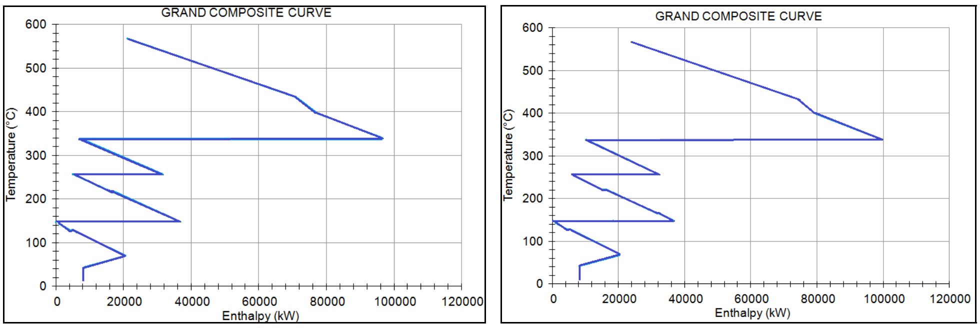

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Figure 6. Grand composite curve for heat recovery from spent air stream (air reactor). a. CLC using ferric oxide; b. CLC using nickel oxide

The grand composite curve shows that a large amount of heating utility with high temperature level is needed in the processes. The cold streams were heated by hot utilities below the pinch, while the hot streams were cooled by cold utilities above the pinch. The pinch analysis indicates that the pinch temperature is around 43°C for CO_2 stream resulted from fuel reactor (Figure 4) and around 147°C for exhaust air resulted from air reactor (Figure 6).

CONCLUSIONS

This paper investigates two oxygen carriers for natural gas chemical looping combustion processes using interconnected fluidized beds with inherent separation of CO_2. The technical evaluation of the processes was based on modeling and simulation work, the most important design characteristics being evaluated in this paper were: general configuration of the CLC system, CO_2 capture rate, heat and power integration issues of the main plant sub-systems, overall energy efficiency, performances of various oxygen carriers etc.

The results obtained after modeling and simulation show that the CLC-technique is a promissing thermo-chemical conversion providing high energy efficiencies in both cases either ferric oxide or nickel oxide as oxygen carriers.

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