Chemical Looping Air Separation (CLAS) for Oxygen production: Thermodynamic and Economic Aspects

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Abstract

A number of conventional and emerging air separation technologies are available today for large-scale oxygen production. These technology platforms are often considered as the energy intensive processes. The increasing demand for the oxygen combined with the need of improved economic performance of such production technologies necessitates the search for alternative methods of oxygen production. Chemical Looping Air Separation (CLAS) is one of these alternatives which can possibly run at relatively lower operating temperature and pressure resulting in lower energy footprints. The present paper describes the results of a comprehensive thermodynamic study conducted on twenty different metal oxides for use in the CLAS process. The study was carried out using Fact-sage and an Ellingham diagram was developed relating the Gibbs free energy of the relevant reactions to temperature for all metal oxide systems. Furthermore, the equilibrium partial pressure of oxygen was calculated at elevated temperatures and the steam/CO_2 requirements were determined for the reduction reactor. Based on this thermodynamic scoping study, oxides of manganese, cobalt, copper, lead and chromium have been found most suitable for the CLAS process. Additionally, other factors such as availability of the metal oxides, their physical properties, reaction kinetics, inventory, mechanical strength, health and safety risks, operating and capital costs have also been qualitatively compared.

Keyword: Chemical looping, Oxygen Production, Oxygen carriers, Thermodynamics

1. Introduction

Oxygen is the second largest-volume chemical produced in the world with a 30% share of the global industrial gas market [1]. It has major commercial applications in metallurgical industry, chemical synthesis, glass manufacturing, pulp and paper industry, petroleum recovery / refining, and health services. Emerging markets for oxygen include advanced power generation systems, such as integrated gasification combined cycle (IGCC), Oxy-fuel combustion and solid oxide fuel cells, SOFC. Oxygen is commonly produced at industrial scales by air separation using cryogenic distillation and adsorption based processes [1]. Advanced technologies such as membrane separation and in-situ air separation are also being developed for small-volume point-of-use oxygen generation [1-2]. While conventional cryogenic and adsorption air separation methods are matured technologies, their energy intensity and high costs can no longer be tolerated under the current economic, energy, and environmental crises. Membrane separation methods whilst less energy intensive remain expensive due to challenges associated with their fabrication, installation and integration. As an alternative, Mogtaderi et. al. [3] proposed a novel chemical looping based process for oxygen production referred to as "CLAS" (Chemical Looping Air Separation). The process has been specifically designed as an air separation platform for integration into advanced oxy-fuel and IGCC systems.

The concept of chemical looping reactions has been widely applied in chemical industries from 19th century [4]. The working principle of the CLAS process is based on the two step redox cycle described by (1) and (2). Selected metal oxides are oxidized in the oxidation reactor and collected oxygen from while fully oxidized oxides are forced to decouple their oxygen in a reduction reactor in the presence of steam/CO_2.

Oxidation

$$Me_x O_{y-2}(s) + O_2(g) \rightarrow Me_x O_y(s) \qquad (1)$$

Reduction

$$Me_x O_y(s) \rightarrow Me_x O_{y-2}(s) + O_2(g) \qquad (2)$$

The advantages of the CLAS process over other known processes are the simplicity of its hardware and operation but more importantly its low energy footprint due to reversible chemical reactions of metal oxide systems at relatively low operating temperatures and pressures. However, similar to other chemical looping based processes, CLAS also faces many challenges among them identifying the most efficient oxygen carrier material.

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The current work mainly describes the results of a thermodynamic scoping study carried out for twenty different metal oxides using the FACT-Sage software package (thermo-chemical equilibrium software). The equilibrium partial pressure of oxygen and the steam/CO_2 requirements have been also calculated at elevated temperatures for all studied metal oxide systems. A number of other factors such as availability, price, pre-processing, mechanical strength, kinetics, health and safety, operating and capital costs were also qualitatively compared and discussed for different metal oxides.

2. Selection of Oxygen Carriers for CLAS

Chemical Looping Air Separation (CLAS) typically employs a dual fluidized bed system where a metal oxide is used as a bed material oxidizing with air in the Oxidation reactor. The oxidized metal is then transferred to the second bed (reduction reactor) and reduced by steam/ CO_2 before being sent back to the air reactor completing the loop. This clearly indicates that oxygen carriers play key role in the process and selection of them is very critical for designing an efficient CLAS process.

Different metal oxides and minerals have been studied as oxygen carriers in the past for Chemical Looping Combustion (CLC) and post CO_2 capture processes [3-5]. However, CLAS is different than conventional CLC and other processes in terms of objective and operational measures as described in Table 1. Running a CLAS system at the high temperature may lead to a high energy requirement for heating up the air (Oxidation reactor) and Steam/CO_2 (Reduction reactor) which may increase the energy usage of the system.

Table 1 Cycling comparison between CLC and CLAS.

Process	Cycles			
	Oxidation		Reduction	
	Medium	High Temperature	Medium	High Temperature
CLC	Air	Achievable as oxidation is always exothermic	with Fuel Solid and Gaseous e.g. Coal, Biomass, Natural gas, Syn gas	Favourable as oxides are reduced by fuel (partly exothermic)
CLAS			with Inerts e.g. steam/CO2	Not favourable as reduction is endothermic

It can be stated from above that unlike CLC, CLAS process should run at lower temperatures. However, lower temperatures may slow down the chemical reaction kinetics and a larger system volume may be needed which will increase capital investment.

Therefore, there is a need to study different oxygen carriers for the CLAS process in terms of their thermodynamic suitability and reaction kinetics at lower temperatures.

2.1. Thermodynamic scoping study

Twenty elements were selected from the periodic table including transition metal elements (e.g. K, Ca, Ce, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ru, Rh, Pd, Pt, Cd, Re, Os, Ir, Pb, Bi) and their different oxidation states were studied using Fact-sage. Results were plotted as an Ellingham diagram in Figure 1. The study was limited to metal oxides only as other potential oxygen carriers such as sulphides, chlorides, nitrites, carbides may generally not suitable for high purity oxygen production using the CLAS process.

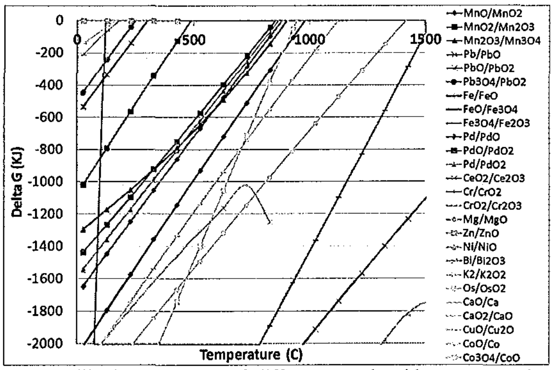


Fig 1. Ellingham diagram of different metal oxide systems using Fact-sage (the diagram does not show metal oxide systems having ΔG lower than -2000 KJ).

The Ellingham diagram plots the standard free energy of reaction as a function of temperature. The Gibbs free energy (ΔG) of a reaction is a measure of the thermodynamic driving force that makes reaction occurs. A negative value for ΔG indicates that a reaction can proceed spontaneously without external inputs. The equation for Gibbs free energy is:

$$\Delta G = \Delta H - T\,\Delta S \qquad (3)$$

where ΔH is the enthalpy, T is absolute temperature, and ΔS is entropy.

The Ellingham diagram can qualitatively suggest whether a given metal system will oxidize, reduce or remain as an oxide or pure metal [6]. However, it does not quantify rate of the reaction. It can be assumed that reaction will qualitatively occur more rapidly as temperature increases or as the conditions for reducing or oxidation deviate farther from equilibrium conditions. Metal oxide systems plotted high up on the diagram are easier to reduce compare to metal oxide systems lower on the diagram and the latter ones are easier to oxidize.

Further, the Equilibrium Partial Pressures of Oxygen for different metal oxide systems at elevated temperatures have been calculated using (4) and plotted in Figure 2. The dotted zone displays the useful metal oxide systems that can run at low temperatures.

$$p_{O_2}\Big|_{eq,T} = \exp\frac{\Delta G^{\circ}}{RT} \quad (4)$$

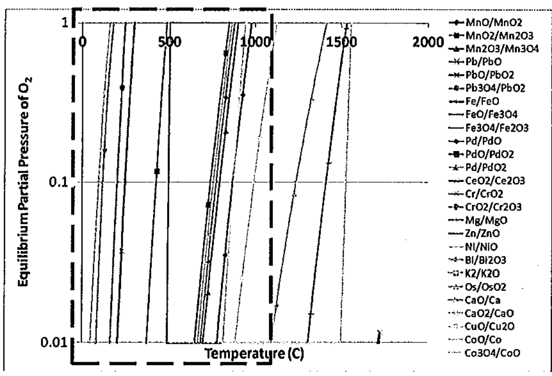


Fig 2. Equilibrium partial pressure of oxygen for different metal oxide systems at elevated temperatures.

According to Le Chatelier's principle, if the equilibrium of the system is disturbed by changing its equilibrium partial pressure or temperature, the system will try to achieve equilibrium and oxidation and reduction can be realized [3].

The oxidation of the selected metal oxide system for CLAS can take place by increasing the actual partial pressure of oxygen above its equilibrium value by providing air. In contrast, the oxygen-releasing step (reduction) can happen by creating a reducing environment using inert (steam/CO_2). The reason for the selection of steam/CO_2 is mainly for the purpose of oxygen purity. However, CO_2 can only be used for oxygen production in an oxy-fuel firing plant where it is recycled in the furnace along with O_2 to maintain the desired flame temperature.

The steam/CO_2 requirements for reduction have been calculated and plotted against the equilibrium partial pressure of oxygen in Figure 3 for Mn_2O_3/Mn_3O_4 system by assuming an actual partial pressure 10% higher and 10% lower than the equilibrium partial pressures of oxygen in the oxidation and reduction reactors respectively.

It can be observed from Figure 3 that running the system at lower temperatures will decrease the equilibrium partial pressure but at the same time significantly increase the inert (steam/CO_2) requirement in the reduction reactor. Furthermore, the kinetics will be slow at lower temperature. However, running the system at high temperature will reduce the oxygen throughput due to increased partial pressure and will increase the energy foot prints.

One of the objectives of this thermodynamic scoping study was to determine the potential metal oxide systems those operate at relatively lower temperatures along with lower steam/CO_2 requirement to reduce the energy foot-print of the CLAS system. Looking to the thermodynamic variables, metal oxide systems in the temperature ranges between 150 ^{o}C to 1000 ^{o}C have been considered as the potential systems for CLAS.

Fig 3. Steam/CO_2 requirement calculations for Mn_2O_3/Mn_3O_4 oxide system at elevated temperature.

2.2. Other Factors

Apart from thermodynamic suitability, other factors are also needed to be considered for efficient process design and operation. Factors that have been qualitatively compared and discussed in this study are shown in Table 2 for selected metal oxide systems.

It can be seen that the oxides of Ca, Cr, Pb and Mn are suitable for redox process at temperatures below than 500 ^{o}C. However, lead oxides due to their higher density will be unfavorable for gas-solid circulation (chemical looping) systems. From the literature, it was found that Calcium peroxide at lower temperatures may be highly unstable. For an intermediate temperature range (650-1150 ^{o}C), oxides of Pd, Mn, Co and Cu appear to be promising in delivering a redox mechanism. However, Pd is rare element and very expensive. Os and Fe are good at high temperatures (>1150 ^{o}C). However, high temperature leads to high energy footprints and capital investment.

From the comparison made in Table 2, it can be observed that oxides of Ca, Cr, Mn, Co and Cu are useful for CLAS operation.

3. Oxygen carrier inventory and steam/CO_2 requirement calculation for CLAS application in oxy-fuel firing thermal power plant

The oxygen carrier inventory and the steam/CO_2 requirement are calculated and presented in Figure 4 for Mn-Oxide systems.

The steam/CO_2 requirements have been assumed and fixed as 2 kg per 1 kg of air using Figure 2 and 3 for calculation purpose in Figure 4. It can be read from the Figure 4 that for such an assumption, the steam/CO_2 requirement (~4000 MT for 500 MW) is significant.

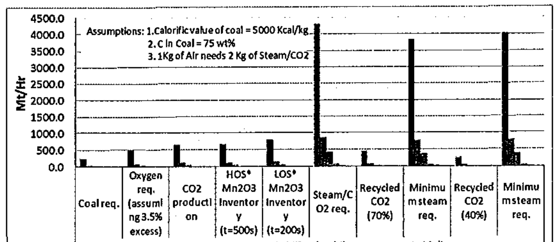
Table 2 Comparison of different Metal oxides as oxygen carriers for CLAS.

	Details	1	2	3	4	5	6	7	8	9	10	11	12	13	14
		CaO/CaO_2	CrO_2/Cr_2O_3	PbO_2/Pb_3O_4	PbO/PbO_2	MnO_2/Mn_2O_3	PdO/PdO_2	Pd/PdO_2	Pd/PdO	Mn_2O_3/Mn_3O_4	CoO/Co_3O_4	CuO/Cu_2O	Os/OsO_2	Fe_2O_3/Fe_3O_4	Pb/PbO
1	Price	Low	Medium	Low	Low	Medium	High	High	High	Medium	Medium	Medium	Expensive	Low	Low
2	Physical Properties														
	Density (g/ml)	3.35 / 2.92	NA / 5.21	9.37 / 9.10	9.53/9.38	5.03 / 4.30	8.70 / Not known	11.40 / Not known	11.40 / 8.70	4.30 / 4.86	6.45 / 6.07	6.40 / 6.00	22.48 / 11.37	5.23 / 5.20	11.34/ 9.53
	Molacular weight	56.07 / 72.07	83.99 / 151.99	239.2 / 685.60	223.2/239.2	86.93 / 157.87	122.42 / 138.41	106.42 / 138.41	106.42 / 122.41	157.87 / 228.81	74.93 / 240.79	79.54 / 143.09	190.2 / 222.20	159.69 / 231.53	207.2 / 223.2
3	Risk (Health and Safety)	Low to Moderate	Moderate	High (Poisonous and Carcinogenic)		Low to Moderate	Low								
4	Operating Temperature (Between 0.001 % to 1 % Eq. PP of O2)	35-150	127-200	200-250	227-300	327-500	627-875	627-875	627-875	627-900	750-950	827-1127	1027-1400	1227-1550	> 1627
5	Reaction kinetics	Slow	Slow	Slow	Slow	Slow	Medium			Medium	Medium	Medium	Fast	Fast	Fast
6	Mechanical Strength	Poor	Medium	High	High	Medium	High			Medium	Medium	Medium	High	Medium	High
7	Solid inventory	Small-Medium	Small-Medium	Small-Medium	Small-Medium	Small-Medium	Small-Medium								
8	Reactor Size	High	High	High	High	High	Medium			Medium	Medium	Medium	High	High	High
9	Steam Separation Unit	Small	Small	Small	Small	Small	Medium			Medium	Medium	Medium	Large	Large	Large
10	Operating Cost	Less	Less	Less	Less	Less	Medium	Medium	Medium	Medium	Medium	Medium	High	High	High
11	Special Remarks	CaO_2 is highly unstable	Poisonous and Lower kinetics	Poisonous, High density and Lower kinetics		Good but possible slower Reaction Kinetics	Too expensive and high density			Good for CLAS operation			Too expensive and high density	High Temperature	High Temperature and high density

Note: Steam separation unit size is qualitatively estimated for fixed steam flow rate with varying temperature.

The amount can be reduced further by increasing the reduction temperature (see Figure 3) but it will reduce the oxygen throughput due to increased partial pressure (see Figure 4). Therefore, it can be stated that the reduction temperature and steam/CO_2 requirement are crucial parameters and needs to be optimised for efficient oxygen production.

Inventory calculations for MnO_2/Mn_2O_3 (HOS) and Mn_2O_3/Mn_3O_4 (LOS) systems suggest that higher oxidation states may be favourable even though having slower reaction kinetics in terms of inventory and energy foot prints due to their lower molar values and lower operating temperature.



	Coal req.	Oxygen req. (assuming 3.5% excess)	CO2 production	HOS* Mn2O3 Inventory (t=500s)	LOS* Mn2O3 Inventory (t=200s)	Steam/CO2 req.	Recycled CO2 (70%)	Minimum steam req.	Recycled CO2 (40%)	Minimum steam req.
500 MW	237.6	494.5	653.4	669.6	803.6	4300.0	457.4	3842.6	261.4	4038.6
100 MW	47.8	98.9	131.4	133.9	160.7	859.9	92.0	768.0	52.5	807.4
50 MW	23.9	49.5	65.7	67.0	80.4	430.1	46.0	384.1	26.3	403.8
10 MW	4.8	9.9	13.2	13.4	16.1	86.1	9.2	76.9	5.3	80.8
5 MW	2.4	4.9	6.5	6.7	8.0	42.9	4.6	38.3	2.6	40.3
1 MW	0.5	1.0	1.3	1.3	1.6	8.5	0.9	7.6	0.5	7.9

Fig 4. Oxygen carrier inventory and steam/CO_2 requirement calculations for oxy-fuel firing thermal power plant (*HOS= Higher oxidation state and *LOS= Lower oxidation state)

4. Conclusion

Comprehensive thermodynamic scoping study was carried for oxygen carrier selection for CLAS. Several other critical factors apart from thermodynamic suitability are also qualitatively compared.

Of the twenty metals with their different oxidation states examined in this study, CaO/CaO_2, CrO_2/Cr_2O_3, MnO_2/Mn_2O_3, Mn_2O_3/Mn_3O_4, CoO/Co_3O_4 and CuO/Cu_2O appear to be potentially suitable for the CLAS process. It was also found that higher oxidation states are generally more favourable as they may operate at lower temperatures with much smaller solid inventories. While not studied here, some metal oxides which exist in the mineral form in nature could also be good option as oxygen carrier in the CLAS process. Solid waste materials such as Municipal Solid Waste (MSW) and coal ash may be also rich sources of metal oxides for the CLAS process.

5. References

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