Exploration of the material property space for chemical looping air separation applied to carbon capture and storage

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HIGHLIGHTS

- Coupling material properties to a steady-state oxy-fuel power plant model.
- A map to estimate *a priori* the performance and viability of redox materials.
- Screening of 2857 candidate materials using large databases of material properties.
- Energy penalty of carbon capture found to be as low as 1.5 percentage points.

ARTICLE INFO

ABSTRACT

Oxy-fuel combustion is one route to large scale carbon capture and storage. Fuel is combusted in oxygen rather than air, allowing pure CO_2 to be captured and sequestered. Currently, the required oxygen is produced *via* cryogenic air separation, which imposes a significant energy penalty. Chemical looping air separation (CLAS) is an alternative process for the production of oxygen, and relies on the repeated oxidation and reduction of solid oxygen carriers (typically metal oxides). The energy efficiency is governed by the thermodynamic properties of the oxygen carrier material, and how well the CLAS process can be heat-integrated with the process consuming oxygen. In this study, key thermodynamic properties have been identified and assessed using a steady state model of a CLAS-oxy-fuel power plant. It is demonstrated that energy penalties as low as 1.5 percentage points can be obtained for a narrow range of material properties. Based on density functional theory calculations, 14 oxygen carrier systems, which are novel or have received little attention, have been identified that could potentially achieve this minimal energy penalty.

1. Introduction

The oxy-fuel process is a promising approach for capturing carbon dioxide from power plants fired with fossil fuels [1]. Here, fossil fuels are burnt in a mixture of CO_2 and O_2, ultimately yielding a stream of CO_2 sufficiently pure for sequestration in geological formations [2]. The cost of the energy required to produce the oxygen needed for combustion is currently a major drawback. Using cryogenic air separation to supply pure oxygen results in a reduction in the net efficiency of a typical power plant of ca. 8–10 percentage points [3–5].

A potential way to overcome this energy penalty is to exploit a technique commonly referred to as chemical looping to separate oxygen from the air. A chemical looping process is characterized by the cyclic reduction and oxidation of solid material, termed here the *oxygen carrier*. The commercial production of oxygen using such a scheme dates back to 1880 when it was successfully realized by Arthur and León Brin [6]. However, one of the drawbacks of the Brin process, which looped between BaO and the peroxide BaO_2, was the need to first remove the carbon dioxide present in the air, which otherwise led to the irreversible formation of $BaCO_3$. Consequently, the Brin process was superseded by the cryogenic separation of air in the early 20th century. In 2000, the idea of exploiting a chemical loop for the separation of air was reintroduced, in this case using a perovskite (LSCF) as the oxygen carrier [7,8]. Later, simpler compounds, such as CuO/Cu_2O, Mn_2O_3/Mn_3O_4 and CoO/Co_3O_4, were considered as oxygen carriers [9,10]. At high temperatures, copper oxide and other transition metal oxides do not react with the CO_2 in air to form stable carbonates under process conditions.

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Nomenclature

CLAS	chemical looping air separation	P_{O_2}	equilibrium partial pressure of oxygen (bar)
		$P_{O_2,air}$	oxygen partial pressure of air (bar)
DFT	density functional theory	$P_{O_2,ox}$	operating partial pressure of oxygen of the oxidizing re-actor (bar)
HRSG	heat recovery steam generator		
LHV	lower heating value	$P_{O_2,red}$	operating partial pressure of oxygen of the reducing re-actor (bar)
LSCF	lanthanum strontium cobalt ferrite		
OC	oxygen carrier	$P_{O_2,req}$	partial pressure of oxygen required by the oxy-fuel com-bustor (bar)
$\Delta C_{p,r}$	molar heat capacity of reaction (J/K/mol)		
ΔG_r^o	Gibbs free energy of reaction at 1 bar (J/mol)	P_{tot}	operating pressure of the reducer (bar)
ΔH_r^o	enthalpy of reaction at 1 bar (kJ/mol)	$\dot{Q}$	heat flow between the oxidizer and reducer (W)
ΔS_r^o	entropy of reaction at 1 bar (J/K/mol)	R	universal gas constant (J/K/mol)
ΔT_{min}	minimum temperature difference in heat exchanger (K)	RH	relative humidity (%)
ΔT_r	temperature difference between oxidizer and reducer (K)	$S_{O_2}^o$	entropy of formation of oxygen at 1 bar (J/K/mol)
$\dot{N}_{solid}$	solids circulation between the oxidizer and reducer (mol/s)	T	temperature (K)
		T_{dew}	dew point temperature (K)
		T_{eq}	equilibrium temperature of the oxygen carrier with oxygen and operating temperature of the reducer (K)
$\dot{N}_{CO_2}$	flow of carbon dioxide from the reducer (mol/s)		
$\dot{N}_{H_2O}$	flow of water separated out in the CLAS condenser (mol/s)	y_i	mole fraction of species i in the gas phase (–)
$\dot{N}_{O_2,ox,in}$	flow of oxygen to the oxidizer (mol/s)	α	ratio of activities of the solids
$\dot{N}_{O_2,red}$	flow of oxygen from the reducer (mol/s)	μ	chemical potential (J/mol)
$\dot{N}_{solid}$	flow of steam from the reducer (mol/s)	χ_{inert}	molar fraction of inert material in the solid phase (–)

A putative process flow diagram for a CLAS-oxy-fuel power plant is shown in Fig. 1. The power plant can be subdivided into three parts: (i) the chemical looping air separation (CLAS) unit, (ii) combustion of the fuel including carbon sequestration, and (iii) a steam cycle for power generation. The flue gas leaving the oxy-fuel combustor will require cleaning to remove particulate matter and sulphurous gases, derived from the fuel. The CLAS unit would consist of two interconnected fluidized beds, *viz.* the oxidizer and reducer [10]. By cycling the oxygen carrier between the oxidizer and reducer, continuous oxygen production can be achieved in the latter. If an existing power plant were to be retrofitted for oxy-fuel combustion, the composition of the incoming oxidizing gas would have to allow the combustor to operate within its envelope of design parameters (*e.g.* to ensure a correct heat transfer coefficient) [11–13]. Accordingly, an oxy-fuel combustor would typically require a mole fraction of oxygen of around 0.3–0.35, with the balance being CO_2 when a dry recycle is used (oxy-dry combustion) [11,12]. The condenser in Fig. 1 allows the mass fraction of oxygen entering the combustor to be altered, by allowing for the removal of water, which may have been injected into the reducer as steam.

The selection and identification of suitable oxygen carrier materials is crucial to the feasibility of a CLAS process. Oxygen carriers must operate at intermediate to high temperatures for a long period of time
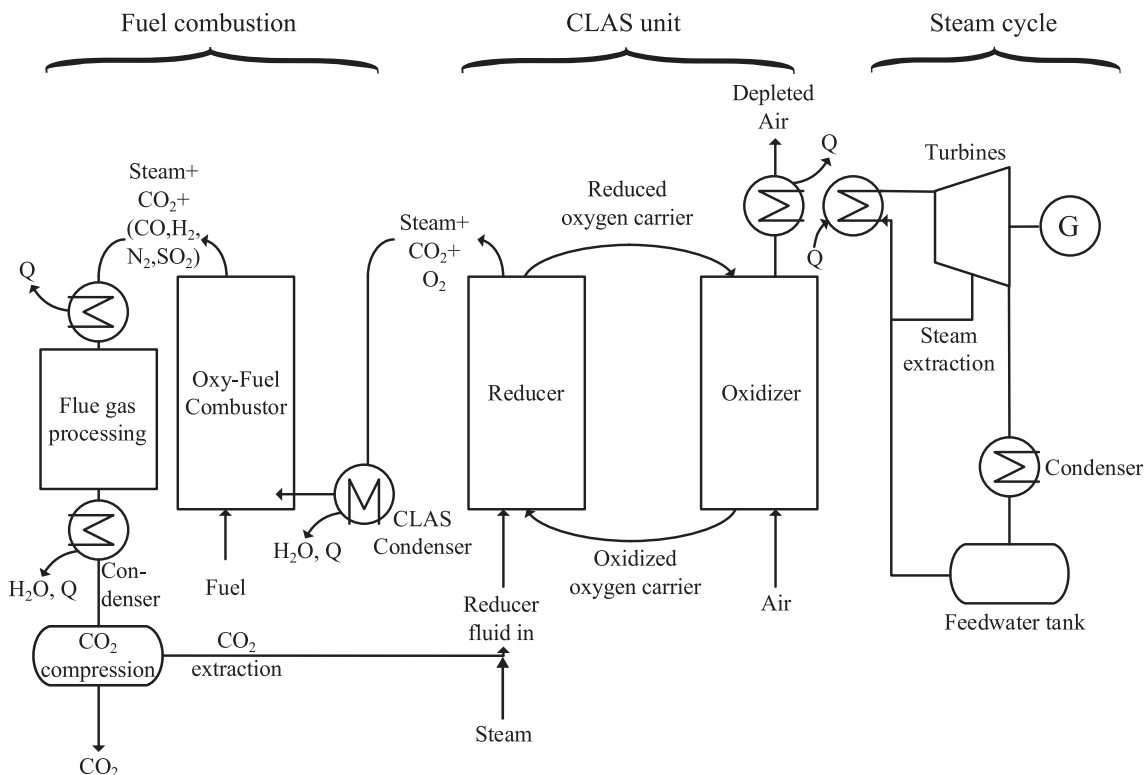

Fig. 1. Flow diagram of a proposed CLAS-oxy-fuel power plant. Q denotes a heat source or sink as indicated by the arrows.