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Simulation of Perovskite Membrane for Integration into a Chemical Looping Air Separation Unit

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The Chemical Looping Air Separation (CLAS) process was developed at the University of Newcastle for tonnage oxygen production. CLAS has a much lower energy intensity than conventional processes, requiring only 12 % of the specific power consumption; however, there are still some energy penalties associated with the CLAS process. The most significant being the large amounts of energy consumed in the steam generation and condensation processes. The aim of this study is to increase the energy efficiency of the CLAS process via membrane integration. If a high temperature oxygen transport membrane is introduced in the reduction reactor of the CLAS system, pure oxygen is produced without the need for a steam condenser. The most attractive oxygen transport membrane is $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}$ (BSCF) owing to its high oxygen permeation flux. The BSCF membrane was utilised to study the oxygen permeation flux, oxygen recovery and energy saving of the integrated process compared to the typical CLAS process. A mathematical model was developed for the BSCF disk membrane to predict the oxygen permeation flux and oxygen recovery over a range of temperatures. Constants of the model were fitted using experimental data. The modelling results showed almost 10 % and 13 % energy savings in the low and high temperature membrane integrated CLAS processes over the typical CLAS, respectively.

1. Introduction

Cryogenic distillation and adsorption based technologies are common air separation units for oxygen production on industrial scales (Kerry, 2007). Although these air separation methods are mature technologies, their high energy intensities can no longer be tolerated under current economic, energy and environmental constrains. There is a need for an alternative air separation technology with a much smaller energy footprint than conventional air separation methods. In recognition of this need, the Chemical Looping Air Separation (CLAS) process (Moghtaderi, 2010) was developed at the University of Newcastle as an alternative air separation process for tonnage oxygen production.

The CLAS process works in a cyclic fashion by continuous circulation of oxygen carriers (typically metal oxides e.g., CuO/Cu_2O) between two fluidised bed reactors (Figure 1). The oxidation (O_2 coupling) and reduction (O_2 decoupling) of oxygen carriers take place in the oxidation and reduction reactors, respectively. Air is fed into the oxidation reactor to regenerate reduced oxygen carriers to a higher oxidation state. The regenerated oxygen carriers are transported back to the reduction reactor where oxygen decoupling occurs in the presence of steam thus releasing the oxygen. For instance, the oxidation and reduction of CuO/Cu_2O are described as Eq(1) and (2). The mixture of steam and oxygen exiting from the reduction reactor passes through a condenser so that steam can be fully separated from oxygen via condensation.

$$Cu_2O + 0.5\,O_2 \rightarrow 2\,CuO \tag{1}$$

$$2\,CuO \rightarrow Cu_2O + 0.5\,O_2 \tag{2}$$

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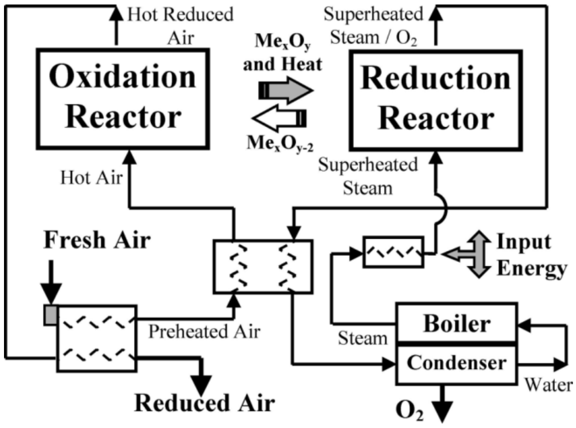

Figure 1: Scheme of the CLAS process (Moghtaderi, 2010)

In order to minimise the energy footprint of the CLAS process (e.g. use of condenser/boiler or air pre-heater), a range of waste heat management techniques are used as shown in Figure 1. However, there is still a need for generation and condensation of steam. If oxygen can be separated without condensing the steam, a significant quantity of thermal energy can be saved. As a result, the overall energy footprint of the process can be reduced. This can be achieved by integrating an oxygen transport membrane into the reduction reactor of CLAS for in-situ removal of oxygen (Paymooni et al., 2013).

The integration of oxygen transport membranes to different processes has been extensively investigated. An integration of polymeric, ceramic and metallic membranes to an Integrated Gasification Combined Cycle (IGCC) system was studied from a CO_2 emissions perspective. Simulation results showed that significant amounts of CO_2 emitted from IGCC can be captured with the use of inorganic membranes (Koutsonikolas et al., 2013). Another study showed a 0.7 % increase in energy efficiency with the integration of oxygen transport membranes into an IGCC system (Anantharaman and Bolland, 2011).

Among oxygen transport membranes, perovskite structures exhibit the best oxygen permeation properties. In terms of their application in the CLAS process, high purity oxygen can be produced as perovskites are exclusively selective for oxygen, among all present gases. This eliminates any need for steam condensation in the CLAS process which results in energy savings. In regards to membrane composition, perovskites with the formula of $ABO_{3-\delta}$ are compounds of interest, where A is occupied by alkali, alkali earth or rare earth metals and B are transition metal cations (Buggraaf and Cot, 1996). Among all perovskite compounds, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) has the highest oxygen flux and has been most widely studied. A long-term oxygen permeation study of disk BSCF membranes showed stable oxygen production for the duration of more than 1,000 h at 850 °C (Shao et al., 2000). BSCF disk membranes with layered morphological structure, named asymmetric membranes, showed even higher oxygen permeation over self-supported membranes (Chen et al., 2007). Permeation flux, oxygen recovery, and oxygen ionic conductivity of dead-end BSCF tubular membranes were studied under pressure-driven, vacuum and a combination of both conditions. Experimental results showed a significantly higher oxygen permeation flux in the vacuum process over the pressure-driven process under similar operating conditions (Liang et al., 2012). Results of the oxygen permeability and oxygen ionic conductivity of tubular BSCF membranes were in agreement with the predictions of the Wagner's theory. Engels et al. (2010) determined coefficients of the Wagner equation for tubular BSCF membranes to study their application in oxy-fuel power plants. A 4-end (i.e., circulating a sweep stream of flue gas) and 3-end concept (i.e., applying vacuum) were simulated using ASPEN software to determine an efficiency of the power plant and membrane area. Results showed a higher efficiency as well as a smaller membrane area for the 4-end process compared to the 3-end (Engels et al., 2010). Even though 4-end design is preferable, only 3-end is technically viable because there is no membrane material which withstands contact with flue gases (Stadler et al., 2010).

The aim of this work was to develop a mathematical model for a BSCF disk membrane which could be integrated into the CLAS process. The parameters of the model were determined using literature-based experimental data. Oxygen recovery was calculated as one of the most crucial parameters impacting on the energy efficiency of the membrane integrated CLAS process.

2. Process simulation

The conventional CLAS and membrane integrated CLAS processes were simulated using ASPEN Plus software version 7.3. Simulations were carried out for the CuO/Cu_2O system at atmospheric pressure and a range of temperatures (850-1,100 °C), assuming 1 kmol/h inlet air. Simulations were aimed to fully convert CuO to Cu_2O to achieve oxygen production. The net heat required for 100 % CuO conversion was determined. A mathematical model was also developed for the BSCF disk membrane to calculate the oxygen permeation flux and oxygen recovery at various temperatures.

2.1 CLAS unit simulation

The CLAS unit was simulated at low (850-1,000 °C) and high (1,000-1,100 °C) temperature ranges. In the Low Temperature CLAS (LT-CLAS) simulation, the oxidation reactor temperature was set at 850 °C. A sensitivity analysis showed that at a reduction temperature of 1,000 °C, 100 % conversion of CuO into Cu_2O was achieved (Paymooni et al., 2013). In the High Temperature CLAS (HT-CLAS) simulation, the oxidation reactor temperature was set at 1,000 °C. Simulation results showed that 100 % CuO conversion was achieved at reduction temperatures equal to or higher than 1,100 °C (Paymooni et al., 2013).

2.2 Membrane unit modelling

Assuming bulk diffusion as the limiting step in oxygen transport across a thick membrane, the Wagner equation (Buggraaf and Cot, 1996) was used to calculate the oxygen permeation flux, j_{O2}:

$$j_{O_2} = \frac{RT}{4^2 F^2 L} \int_{\ln P_{O2}''}^{\ln P_{O2}'} \frac{\delta_e . \delta_i}{\delta_e + \delta_i} \, d \ln P_{O_2} \tag{3}$$

where R, F, L, δ_e, δ_i, P'_{O2}, P''_{O2}, are the gas constant, Faraday's constant, membrane thickness, electronic conductivity, ionic conductivity, oxygen partial pressure on the feed side and oxygen partial pressure on the permeate side. The Wagner equation can be simplified into Eq(4) by considering the following assumptions:

- Oxygen vacancy is the only mobile charge through the membrane
- Electron conductivity is much higher than ionic conductivity
- Vacancy diffusion coefficient is only temperature dependent
- Arrhenius equation can be used to calculate E_D

$$j_{O_2} = C \exp\left(\frac{-E_D}{RT}\right) \ln\left(\frac{P_{O_2}'}{P_{O_2}''}\right) \tag{4}$$

where C is the material constant and E_D is the activation energy. The oxygen permeation flux is assumed to be a function of two independent variables, temperature and pressure, Eq(5).

$$j_{O_2} = f\ (T, P) \tag{5}$$

An error minimization method was used to fit the constants (Eq(4)) C and E_D using literature-based experimental data for BSCF disk membrane with the thickness of 1 and 1.5 mm. A relative percentage error between the experimental data and modelling results was calculated to check the accuracy of the model.

2.3 Oxygen Recovery

Oxygen recovery is one of the most important parameters in a large scale oxygen production unit (Liang et al., 2012). The oxygen recovery was calculated using Eq(6) where F_{O2} is the oxygen permeation flow rate and C_{O2} is the volumetric oxygen concentration in the feed (Liang et al., 2012).

$$O_{2,recovery} = \frac{F_{O_2}}{F_{inlet} . C_{O_2}} \tag{6}$$

3. Results and discussion

In this section, the obtained model constants and the oxygen recovery of the BSCF disk membrane are presented. The energy efficiency of the membrane integrated (MI) CLAS process is also discussed.

3.1 Model constants

An error minimization method was used to fit constants of the derived Eq(4) with the literature-based experimental data over a range of temperatures for the membrane thickness of 1 and 1.5 mm. The experimental data and the obtained constants are reported in Tables 1 and 2.

Table 1: Experimental data for the BSCF disk membrane, L=1.5 mm and L=1 mm.

L, mm	T, °C	J_{O2}, mL.cm^{-2}.min^{-1}	
1.5	600-950	0.06-1.57	(Shao et al., 2000)
1.5	600-950	0.10-1.60	(Shao et al., 2001)
1.5	700-900	0.62-1.74	(Wang et al., 2005)
1.0	700-900	1.21-3.02	(Chen et al., 2007)
1.0	700-950	0.86-2.55	(Behrouzifar et al., 2012)

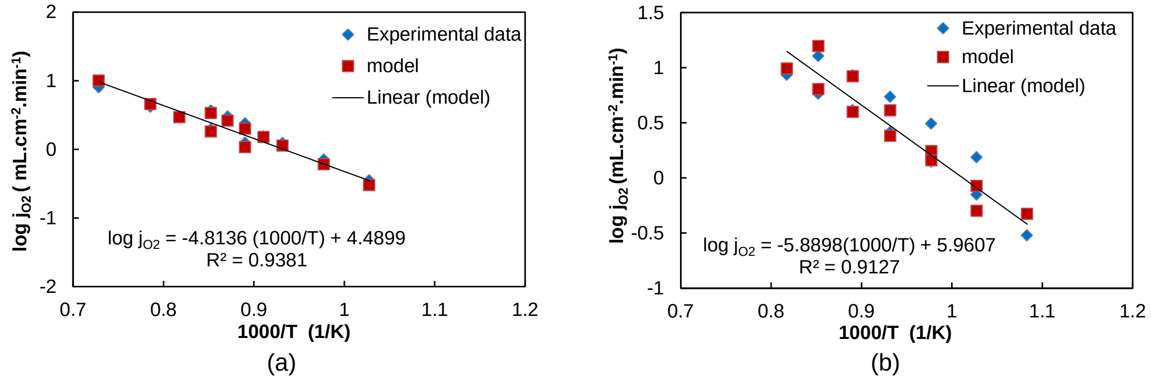

Figure 2: Logarithmic function of oxygen permeation flux across BSCF disk membrane for (a) L=1.5 mm and (b) L=1 mm

Table 2: Calculated constants of simplified Wagner equation Eq(4).

L, mm	C, mol. cm^{-2}.s^{-1}	E_D, kJ.mol^{-1}
1.5	9.09×10^{-5}	49.72
1.0	1.56×10^{-4}	56.16

The logarithmic functions of oxygen permeation flux at different temperatures for 1 mm and 1.5 mm thick BSCF disk membranes were plotted in Figures 2 (a) and (b). As seen, good agreement was achieved between the experimental data and the calculated oxygen permeation flux according to Eq(4).

3.2 Oxygen recovery

The calculated oxygen recovery of the CLAS process under equilibrium conditions and the BSCF disk membrane are reported in Tables 3 and 4. The equilibrium volumes of the produced oxygen in the reduction reactor of CLAS at different temperatures are reported by Moghtaderi (2010). Literature-based experimental data (Shao et al., 2000) as well as the predicted oxygen permeation flux by Eq(4) in the temperature range of 850-1,100 °C (maximum operating temperature of the membrane) were used to calculate the oxygen recovery of the BSCF disk membrane. The calculated percentage relative error represented a good agreement between the predicted oxygen permeation flux using Eq(4) and the reported experimental data by Shao et al. (2000).

Table 3: Calculated oxygen recovery of the CLAS process

T, °C	Oxygen volume [a], m^3.h^{-1}	$F_{Air}.C_{O2}$, m^3.h^{-1}	$O_{2,\ Recovery}$ (%)
850	4.89	4.89	100
900	4.65	4.89	95
950	2.69	4.89	55
1,000	2.20	4.89	45

[a] Equilibrium oxygen production reported by Moghtaderi (2010).

Table 4: Calculated oxygen recovery of the BSCF disk membrane, A = 0.85 cm^2, L = 1.5 mm, $F_{Air}.C_{O2}$ = 30 mL.min^{-1}

T, °C	J_{O2}, Experimental [b] mL.cm^{-2}.min^{-1}	J_{O2}, Model [C] mL.cm^{-2}.min^{-1}	Relative error (%)	$O_{2, Recovery}$ (%)
850	1.11	1.03	6.01	17.9
900	1.34	1.29	3.19	21.5
950	1.59	1.59	0.49	25.6
1000	-	1.93	-	31.1
1100	-	2.72	-	43.7

[b] Shao et al., 2000
[C] Calculated with Eq(4).

Comparison between the oxygen recovery of the BSCF membrane and the CLAS process is illustrated in Figure 3. As the BSCF membrane is integrated into the reduction reactor of the CLAS, the oxygen recovery of the BSCF membrane plays a crucial role in the energy efficiency of the integrated process. The oxygen recovery of the BSCF disk membrane increases with temperature to its maximum of 43.7 % due to an increase in an oxygen flux with temperature. However, a decreasing trend is seen for the CLAS process as the volume of oxygen production decreases with an increase in temperature. This can be justified by the fact that at higher reaction temperatures, lower oxygen is produced due to equilibrium constrains (Moghtaderi, 2010).

3.3 Energy efficiency

The membrane integrated CLAS systems were studied from an energy savings perspective under ideal (i.e., 100 % oxygen recovery via BSCF membrane) and practical (i.e., practical recovery calculated using Eq(4)) conditions. Under ideal conditions, the required heat for LT-CLAS, HT-CLAS and the MI-CLAS processes were calculated. According to the results, reported in Table 5, an energy saving of 30 % was achieved via membrane integration into the CLAS process under ideal conditions.
However, the energy savings of the LT and HT membrane integrated CLAS processes decreased from 30.8 % and 29.5 % under ideal conditions to 9.58 % and 12.9 % under practical conditions as reported in Table 6. A decrease in energy savings under practical conditions is due to a decrease in the oxygen recovery from 100 % to the reported values in Table 4.

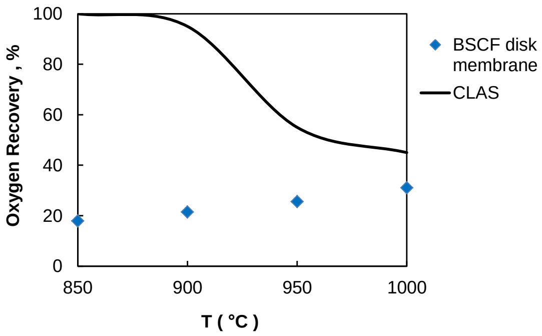

Figure 3: Comparison between the calculated oxygen recovery of the BSCF disk membrane and the CLAS process

Table 5: Required heat for CLAS and membrane integrated CLAS systems under ideal conditions (Paymooni et al., 2013)

Cases	T $_{Oxidation\ reactor}$, (ºC)	T $_{Reduction\ reactor}$, (ºC)	Q $_{Net}$, [kW/(kmol.h^{-1})$_{air}$	Energy Savings
LT-CLAS	850	1,000	5.12	-
MI- LT CLAS	850	1,000	3.54	30.8%
HT- CLAS	1,000	1,100	6.39	-
MI- HT CLAS	1,000	1,100	4.50	29.5%

Table 6: Energy savings of membrane integrated CLAS systems under practical conditions

Cases	$T_{\text{Reduction reactor}}$, (°C)	Energy Savings ideal	$O_{2,\text{Recovery}}$ BSCF	Energy Savings practical
MI- LT CLAS	1,000	30.8 %	31.1 %	9.58 %
MI- HT CLAS	1,100	29.5 %	43.7 %	12.9 %

4. Conclusions

In this study, a membrane integrated CLAS process was proposed as a promising energy efficient air separation unit. The BSCF membrane was selected for integration into the CLAS process. A mathematical model was developed for the BSCF disk membrane assuming bulk diffusion as the limiting step in oxygen transport through the membrane. Constants of the model were fitted using literature-based experimental data. The oxygen recovery of the BSCF disk membrane was determined due to its impact on the oxygen production in the integrated configuration from an energy efficiency perspective. The energy savings of the membrane integrated CLAS process are almost 10 % and 13 % at low and high temperature ranges, respectively, over the typical CLAS process. Although the MI-CLAS process is viable from an energy efficiency perspective, the membrane area and geometry should be engineered in future studies to evaluate the economical feasibility of the proposed process.

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