CHALMERS

Assessment of a proposed fluidized-bed air separation process

Master's Thesis within the Sustainable Energy Systems and Innovative and Sustainable Chemical Engineering programmes

CIM KOLHAMMAR
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MASTER'S THESIS

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Abstract

This report investigates the eligibility of oxygen carrier materials of oxygen-uncoupled nature (exemplified by the metal complex CuO/Cu_2O) for air separation, with focus on the power industry and oxy-fuel combustion. The influence of a number of parameters is assessed and attempts of process integration reported. The cost of producing a given flow of oxygen in terms of fuel, heat and electricity required is reported and compared with that of conventional cryogenic air separation.

At a given temperature, the investigated metal complex has an equilibrium relation with the partial pressure of oxygen in the surrounding gas. By varying either temperature or pressure, the metal complex may release or capture oxygen from the surrounding atmosphere. This behavior, on which chemical- looping with oxygen uncoupling (CLOU) is based, is utilized for air separation in the present work.

Four different process integration setups of the proposed air separation unit (ASU) are investigated and the resulting energy penalty is compared to the corresponding energy penalty of a cryogenic ASU. Three of the investigated process integrations produce an O_2/CO_2 mixture suitable as inlet stream in oxy-fuel combustion units while the fourth produces an $O_2/steam$ mixture which is later condensed to produce pure O_2.

One of the process integration setups (with an O_2/CO_2 mixture as product) includes indirect heat exchanging of the proposed ASU, while the others did not. The remaining two O_2/CO_2 process integration setups only heat exchanges in- and outgoing streams (not the ASU itself). One of these two O_2/CO_2 setups operates at ambient pressure while the other has a slight overpressure in one of the two reactors. All O_2/CO_2 setups achieve higher thermal efficiencies than the reference case with cryogenic ASU. The thermal efficiency of the process integration setup producing $O_2/steam$ is much lower than its reference case with cryogenic ASU.

The proposed process does not require such heavy cooling or compression as the conventional cryogenic air separation unit dominating the market today. On the other hand, the proposed ASU works at high temperatures and requires extensive heat recovery to maintain good thermal efficiencies when process-integrated. This requires resilient heat exchanger materials, as well as large heat exchange areas as both mediums involved are gaseous. These facts limit the eligibility of the process, as the gains in thermal efficiency might be offset by the increase in maintenance and capital cost for high temperature gas/gas heat exchangers.

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Abbreviations

ASU   Air separation unit

CCS   Carbon capture and storage

CLC   Chemical-looping combustion

CLOU   Chemical-looping oxygen uncoupling

Cryo   Cryogenic

CSTR   Continuously stirred tank reactor

DH   District heating

IGCC   Integrated gasification combined cycle

RFG   Recycled flue gas

SG   Steam generation

Background

Coal is an abundant and available fuel and is therefore likely to continue to play a role as an important energy resource for years to come. A systematic increase of the CO_2 concentration in the Earth's atmosphere is, however, a consequence of burning fossil fuels, unless the emissions are captured and stored. On a dry basis, the outlet stream from conventional combustion is mainly a mixture of nitrogen and CO_2; as can be seen in Figure 1a. Separating CO_2 from such a stream is costly while, as seen in Figure 1b, the outlet stream from oxy-fuel combustion ideally contains nothing but CO_2. This makes oxy-fuel combustion one of the most promising technologies for CO_2 capture, despite the energy penalty coupled to the required air separation.

a)   b)
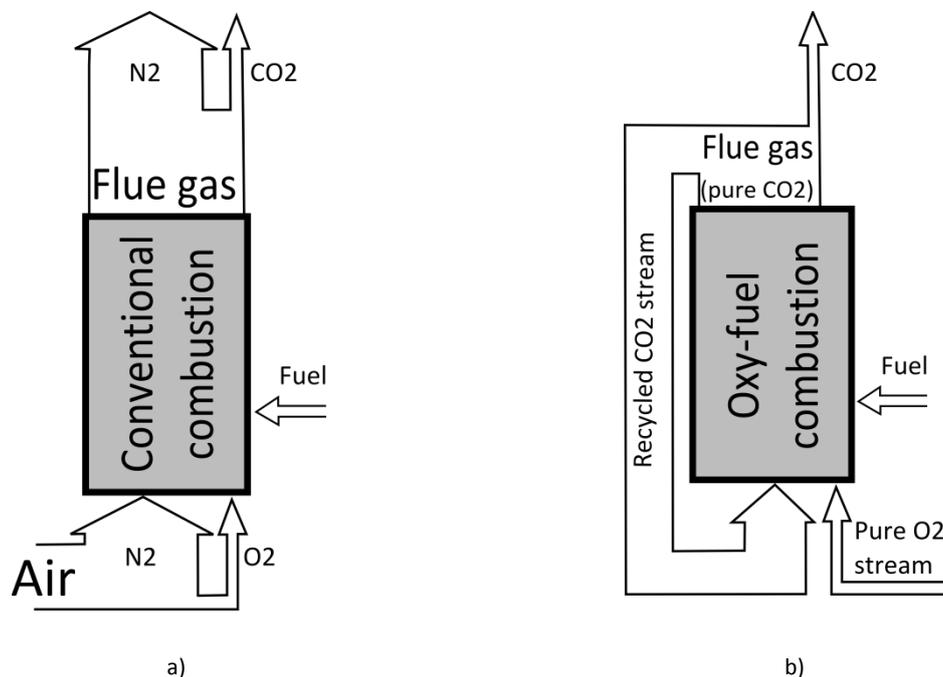
Figure 1: Gas flows (dry basis) in a) conventional combustion and b) oxy-fuel combustion

Currently, air separation is dominated by cryogenic technology. Cryogenic air separation units (Cryo ASU) produce oxygen of high purity (see Figure 2a) by distillation of air at elevated pressures and very low temperatures (Figure 3a). This operation requires a substantial amount of energy even with a high degree of process optimization, and reduces the overall efficiency of an oxy-fuel power plant with 7 to 9 percentage points [1] compared to a conventional power plant. Also, for oxy-fuel to be competitive, the cost of emitting CO_2 will have to be considerable to make up for the loss in efficiency. Furthermore, Cryo ASU is a mature technique and little progress can be expected in terms of efficiency. Thus, step-change alternatives are generally believed to pave the way for large scale CO_2-capture in the long term [2].

Aim

This work investigates the possibility of reducing the energy penalty of oxygen production for oxy-fuel combustion by proposing an innovative air separation process. Furthermore, the influence of operating parameters on the performance of the proposed air separation process is investigated. The

proposed process is a chemical-looping with oxygen uncoupling air separation unit (CLOU ASU). This process supplies the combustion with an $O_2/CO_2/H_2O$ mix where oxygen concentrations are adjusted to fit the target combustion process. With this, the peak in the purity profile (Figure 2a) and the dip in the temperature profile (Figure 3a) coupled to the Cryo ASU can be avoided (Figures 2b and 3b respectively).
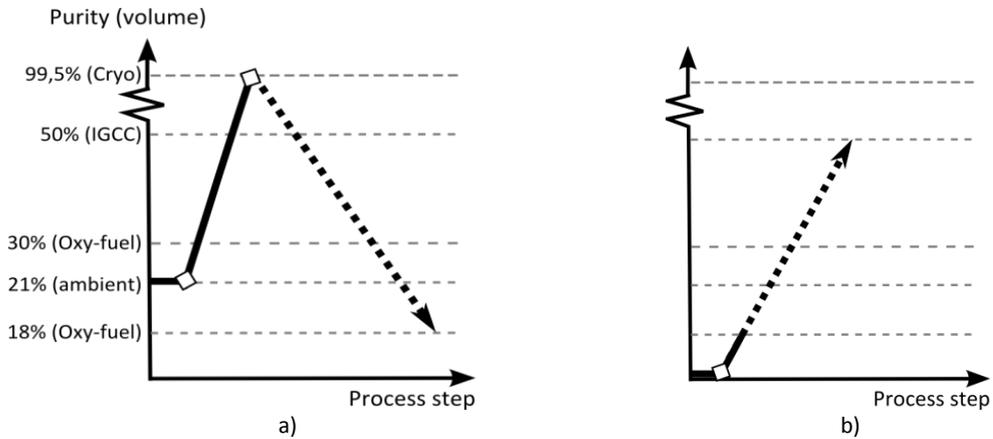
Figure 2: Purity profiles for oxygen production with a) Cryo ASU and b) CLOU ASU applied to power processes. Solid line denotes default oxygen concentration regardless of target process, while the dotted line denotes O_2 concentration adaption for the target process
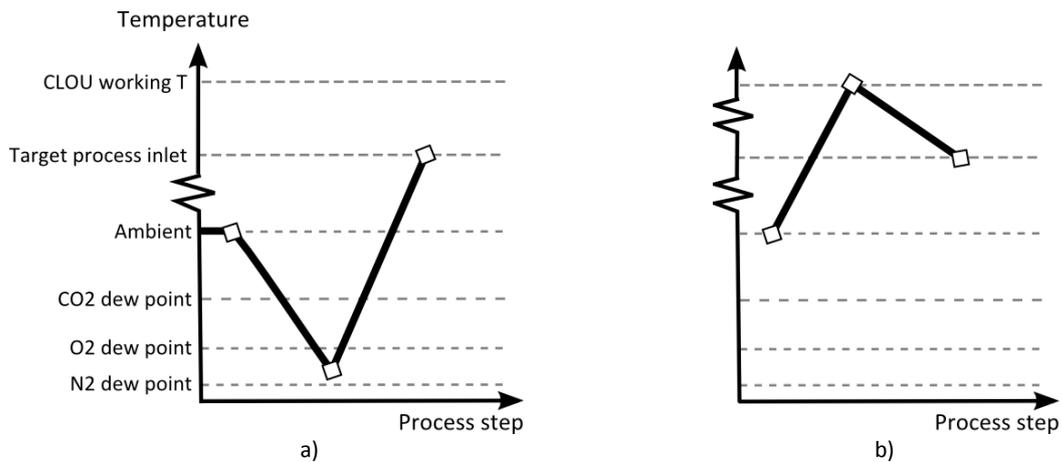
Figure 3: Temperature curves of a) Cryo ASU and b) CLOU ASU applied to a power process

In order to investigate the eligibility of the CLOU ASU in comparison with the cryogenic alternative, a basic model with influential parameters and suitable limitations is required. In the end when the inter-dependence of the different parameters, the limitations of the system, the required concentration and the economy are considered, the eligible region for the CLOU ASU process is much smaller than the physically feasible region, as pictured in Figure 4.
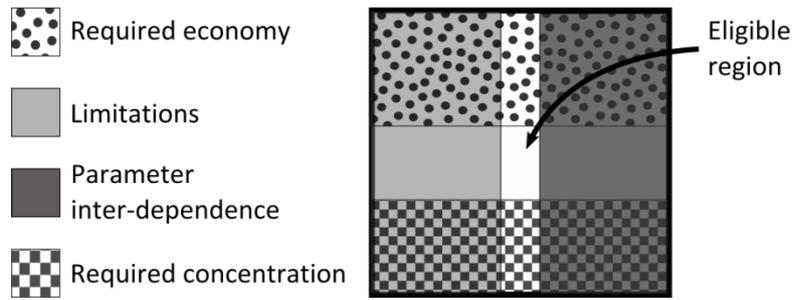
Figure 4: The possibilities of the process narrowed down by four major reasons

Disposition of the work

The theory behind chemical-looping with oxygen uncoupling and the equilibrium behavior of the active metal complex is discussed in the Theory chapter. Later, in the Method chapter, the model design for the air separation unit (as well as its iteration design) is described in detail alongside the process integration model. Finally, the resulting trend graphs are analyzed in the Results and Discussion chapter, to determine the tuning parameter's influence on the output of the CLOU ASU process. This chapter also includes an evaluation of the energy penalties for four different integration cases with the proposed ASU compared to a reference with a Cryo ASU.

Theory

This chapter provides the theory required to investigate the fluidized bed-based CLOU ASU; from the concept of chemical-looping to the importance of the chemical properties of the particles and the distribution of the flows.

The proposed CLOU ASU consists of two interconnected fluidized bed reactors (called capturer and releaser) with a solids flow circulation, as outlined in Figure 5. Oxygen is transferred between the beds by the circulating metal particles, which are oxidized by the inlet air flow inside the capturer and then reduced by the flue gas flow inside the releaser. In that way, a gas mixture leaves the releaser which contains nothing but oxygen and flue gas, i.e. suitable for the oxy-fuel process.
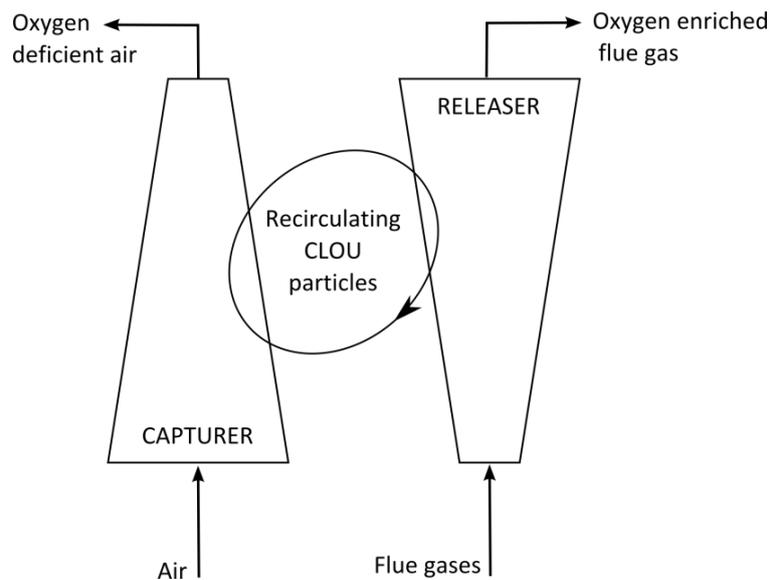
Figure 5: Concept flow sheet of a chemical-looping oxygen uncoupling ASU (CLOU ASU)

Chemical-Looping Technology

The air separation technology investigated in this report uses chemical-looping, a fairly new but promising technique for power production endowed with CO_2 capture equipment [3]. The principles of the technique and its variants are further presented below.

Chemical-Looping Combustion

The concept of chemical-looping combustion (CLC) is a promising alternative to oxy-fuel combustion as a CCS technology, this since the energy penalty associated with air separation is avoided. The technique is based on the ability of certain metal complexes to bind oxygen present in the gas around them (such as air, for instance) to their surface. At high enough temperatures (or, obviously, in oxygen-free environments) the particles will not bind any oxygen and remain in the reduced state depicted in Figure 6a. If exposed to oxygen under the right conditions, the metal complex particles will oxidize to a certain degree up to saturation, see Figure 6b. These two abilities are the underlying foundation of the chemical-looping concept. For structural stability, these oxygen-carrying particles are essentially a mix between inert material and active metal complex.
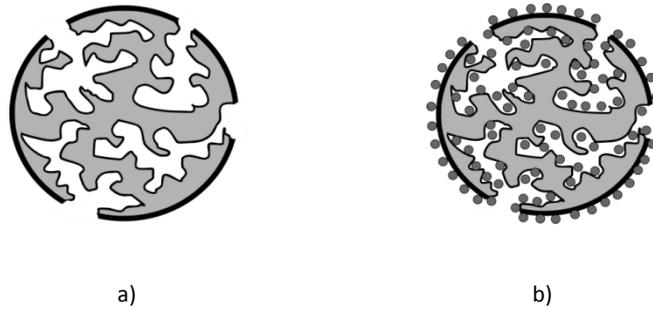
Figure 6: Concept picture of a) completely reduced particle and b) completely oxidized particle

The Chemical-Looping Combustion Process

To separate oxygen from air, the reactor in which particles bind oxygen (called the Air-reactor) must be separated from the reactor in which combustion takes place (called the Fuel-reactor). In CLC this is achieved by connecting two fluidized beds (Air-reactor and Fuel-reactor) through a series of gas seals (see Figure 7) which prevent gas leakage between the two reactors. The oxygen-carrier material is oxidized in the Air-reactor and circulated into the Fuel-reactor, where the oxygen rich particles mix with fuel and combustion takes place on their surfaces. The flue gases leaving the Fuel-reactor are cooled to remove any water produced in the combustion. Once the water is condensed the gas should, depending on the fuel composition, consist mainly of CO_2 which is compressed and cooled in several steps. Once the CO_2 is in liquid form, non-condensable gases are returned to the reactor system and gradually vented out with the reduced air to avoid accumulation.
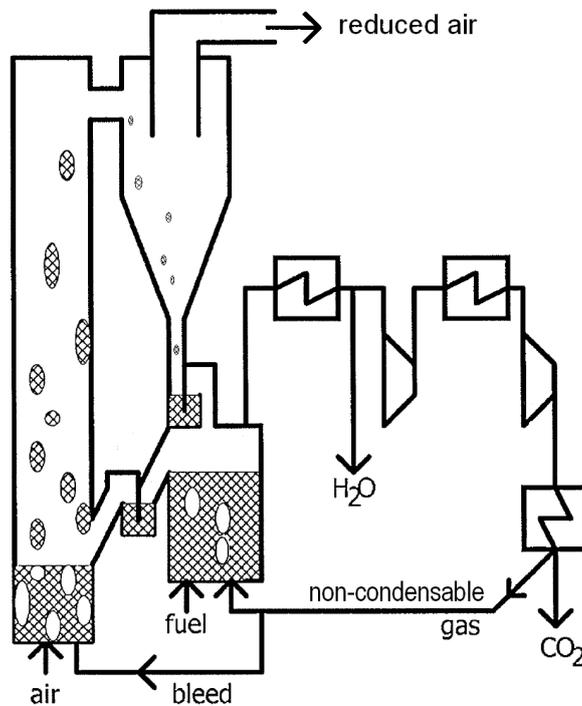
Figure 7: Schematic of a dual fluidized bed, here including water removal, compression and separation of the CO_2 stream. In this example, the Air-reactor is a circulating fluidized bed and the fuel reactor a bubbling fluidized bed.

A problem with CLC is the properties, or robustness, of the oxygen carriers used. Combustion taking place at their surface results in high temperatures which the metal complexes must be able to withstand without sintering, breaking or melting. Also, some compounds present in the fuel or in the combustion products may clog the oxygen capturing surfaces of the porous particles. Another issue is the limitation of the kinetics of the combustion reaction with oxygen on the particle surface. The number of available suitable fuels, or the preferred gaseous form of a common fuel such as coal, is also a concern which limits the prospects of CLC.

Chemical-Looping with Oxygen Uncoupling Combustion

Chemical-looping with oxygen uncoupling, or CLOU (a term established by Mattisson et al. [4]) is a process where, given the proper conditions, metal oxides release the carried oxygen. In the CLOU application suggested by Mattisson et al., the metal particles are oxidized in an Air-reactor and reduced in a Fuel-reactor in which combustion of solid fuels takes place. The need for gasification of the fuel is then removed and the reaction rate is approximated to be 50 times higher for petroleum coke when using CLOU compared to CLC [3]. The amount of suitable oxygen carriers is more limited in CLOU than in CLC as these must be able to actively release oxygen (compared to CLC in which the combustion consumes surface-bound oxygen).

Chemical-Looping with Oxygen Uncoupling ASU

A unit which, similar to the CLOU concept, extracts oxygen from the ambient air in one reactor, and releases it in another reactor, but without the addition of fuel to the system would then work as an air separation unit (ASU). Such a CLOU ASU process should be less affected by fouling and strain on the oxygen carrying particles then a CLOU combustion unit, as well as be able to provide a number of different processes already in place with a gas-mixture free of nitrogen compounds. Such a mix would, after combustion, ideally contain nothing more than CO_2 and/or H_2O, the latter of which may easily be condensed and separated, leaving a clean stream of CO_2 ready for compression and sequestration. The concept has been previously discussed [5].

As can be seen in Figure 5, the air enters the capturer, in which CLOU particles pick up some of the available oxygen. The air exits the capturer somewhat oxygen deficient. The CLOU particles are now oxidized and flow into the releaser. Flue gases enter the releaser, in which the CLOU particles release their oxygen, thereby creating an oxygen-enriched flue gas. The reduced CLOU particles are returned to the capturer, closing the chemical loop.

The Influence of Equilibrium on the Process

Theoretically, CLOU particles could release oxygen to make up almost all of the gas in the releaser. However, the physical properties of the particles, as well as the achievable temperature in the CLOU process limit this in practice. Figure 8 shows the equilibrium O_2 concentration of three metal complexes at different temperatures. For copper the equilibrium temperature at 0.21bar partial pressure of oxygen is 1029°C. Thus, at temperatures below 1029°C, the copper complexes strive to decrease the O_2 concentration around them below the ambient 21vol% (i.e. 0.21bar at atmospheric pressure) and will attempt to do so by binding oxygen until the equilibrium partial pressure is reached or until the particles are saturated (see Figure 6b). On the other hand, at temperatures above 1029°C the copper particles will, if possible, release oxygen until a partial pressure of oxygen higher than ambient is reached in the gas surrounding them. Therefore, in order to transfer as much oxygen from one reactor to another, the temperature should be low in the O_2-capturing reactor

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(capturer) and high in the O_2-releasing reactor (releaser). It is, however, not only a matter of temperature but also of the flow of oxygen-free flue gas entering the releaser. Oxygen saturated copper particles entering the releaser would only be completely reduced (see Figure 6a) at large flows of flue gas and/or temperatures in the vicinity of 1100°C (as seen in Figure 8). Thus, a certain O_2 partial pressure in the gas exiting the releaser can be achieved by adjusting the amount of circulating particles, the temperature and the incoming flow of flue gas.
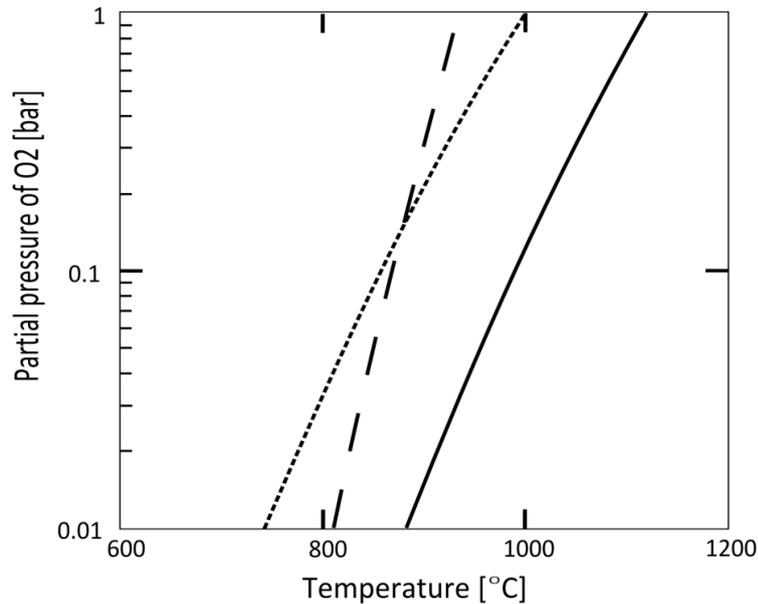
Figure 8: The partial pressure of gas-phase O_2 in bars over the oxygen carrier systems CuO/Cu_2O(—), Mn_2O_3/Mn_3O_4(----) and Co_3O_4/CoO(——) as a function of temperature [3]

In principle, three types of oxygen carrying materials could be applied in the process. These are simple complexes based on copper, cobalt and manganese respectively. Equations 1 to 3 show the forms and heat of reaction of the three materials.

$$4CuO \leftrightarrow 2Cu_2O + O_2(g) \qquad \Delta H_{850} = 263.2 \frac{kJ}{mol} O_2 \qquad \textbf{(1)}$$

$$2Co_3O_4 \leftrightarrow 6CoO + O_2(g) \qquad \Delta H_{850} = 408.2 \frac{kJ}{mol} O_2 \qquad \textbf{(2)}$$

$$6Mn_2O_3 \leftrightarrow 4Mn_3O_4 + O_2(g) \qquad \Delta H_{850} = 193.9 \frac{kJ}{mol} O_2 \qquad \textbf{(3)}$$
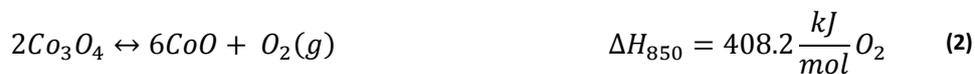
Equations 1 to 3 show that the choice of carrier type affects the required weight of carrier per mole oxygen transferred, as well as the heat balance inside both capturer and releaser (as the heat of reaction differs between carriers). The complexes also respond differently to the surrounding temperature and pressure as displayed in Figure 8.

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Table 1 summarizes the working temperature regions for copper, cobalt and manganese respectively. At the start temperature, the equilibrium curve of the metal complex begins to climb faster toward higher partial pressures of oxygen, and at the end temperature a partial pressure of about 1bar is reached, i.e. 100vol% O_2 at ambient pressure.

Table 1: Temperature regions of interest at 1bar for three different carriers [3]

Metal complex	CuO/Cu_2O		Co_3O_4/CoO		Mn_2O_3/Mn_3O_4	
Interval	Start	End	Start	End	Start	End
Celsius [°C]	800	1100	750	950	650	1000
Kelvin [K]	1073	1373	1023	1223	923	1273

As seen both in Figure 8 and Table 1, the temperatures of interest vary with the carrier. This is also an interesting situation as it implies that different carriers could be used to meet different demands. However, there are in fact many parameters influencing the behavior of the separation unit as a whole, and they will be discussed further in the Results section.

Capturer

The capturer is the fluidized bed where CLOU particles are to bind O_2 from the air flow fluidizing the bed. Being the source of O_2 extraction, this air flow must be sufficiently large to cover the demand set by the releaser. Large flows of carrier metal in comparison to the air flow lead to only partial saturation of the particles, while smaller flows of carrier metal imply a higher degree of saturation under the same conditions. Given a limited flow of carriers, as the temperature increases they will eventually cease being the limiting factor and instead it will be the equilibrium that limits the O_2 capture from ambient air, as schematized in Figure 9. It must be noted that, at high enough temperatures and ambient pressure, the equilibrium curve will encourage the CLOU particles to release any carried O_2 to increase the partial pressure of O_2 around them above the ambient concentration of 0.21bar. If this occurs in the capturer, the purpose of the ASU is lost as no O_2 will be captured and the carriers will attempt to get reduced instead of oxidized.
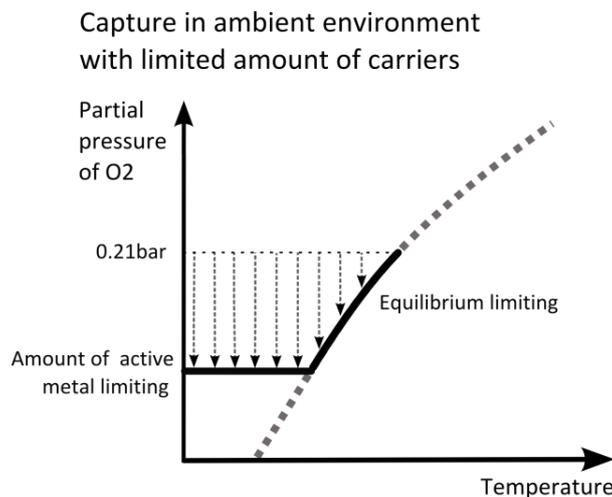
Figure 9: The resulting partial pressure curve due to equilibrium and a limited amount of active metal complexes inside the capturer

Releaser

The releaser is the fluidized bed reactor where oxygen-carrying particles are to release oxygen to the flue gases flowing through the bed. The gas mixture leaving the releaser should ideally be free of nitrogen compounds and may, as described below, either be fed directly in an oxy-fuel process or further separated to achieve higher oxygen concentrations. The limitations connected to the releaser are mainly due to temperature sensitivity of the particles, their equilibriums and the equipment material. Small gas flows into the releaser yield a higher O_2 concentration at the exit, limited only by the amount of available O_2 carried in from the capturer and the equilibrium (i.e. the temperature and pressure inside the releaser).
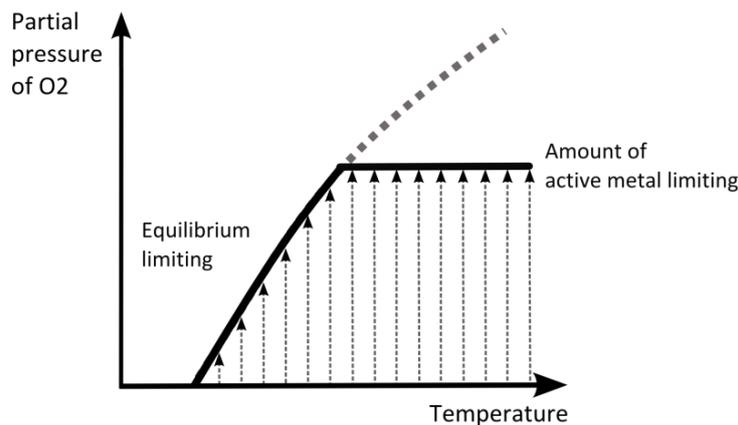
Figure 10: The resulting partial pressure curve due to equilibrium and a limited amount of active metal complexes inside the releaser

Influence of Equilibrium in Practice with CuO/Cu₂O

By heating the releaser, the equilibrium is pushed toward a higher concentration of O_2 in the flue gas, e.g. at 1bar the required temperature to reach 30vol% O_2 concentration (one of the targets for oxy-fuel) is 1049°C for the copper setup. However, copper particles cannot withstand temperatures higher than about 1200°C, and so the desired outlet temperature interval is set by equilibrium and material limitations.

Given a certain amount of carrier particles, the equilibrium will be limiting the amount of O_2 released at low temperatures. On the other hand, at high enough temperatures, the flow of active metal will be limiting (due to that all the active metal has been reduced and is unable to release any more O_2, as derived from Figure 10). This behavior has a major influence on the model, and it requires knowledge about the prevailing conditions inside the reactor to describe it properly. That is, the mass and energy balances depend on *but also influence the behavior of* the curve in Figure 10, as illustrated further in the Method chapter.

Method

The investigation is divided into two parts. The first part is comprised of modelling of the air separation process in Matlab. This model was used to determine whether or not air separation by oxygen carriers could reach sufficiently high concentrations and flows of oxygen to compete (or combine) with the commercially established cryogenic alternative. The model provided data which

was used to clarify the influence of different parameters on the air separation process, e.g. the concentration of oxygen out of the releaser.

The second part consists of modelling of the process integration and is implemented in Ebsilon Professional to investigate the amount of energy required to produce given flows of pure or diluted oxygen streams. To do this, a user-defined module representing the air separation process had to be implemented. The software enables analysis of to which extent in- and outgoing streams may be heat exchanged with each other, as well as the required compressor work or heating through a furnace. The software was also used to quantify possible benefits to be gained through, for instance, application of district heating.

The Project Scope

In this work, certain aspects of the processes were not taken into consideration or investigated in detail. It is assumed that solids flows of any magnitude can be circulated around the reactor system. The size of equipment and heat exchanging area required are not calculated. Finally, temperature limitations set by the equipment are not accounted in detail but only roughly.

Applied Assumptions

A steady state model was used to model the CLOU ASU which solves the energy and mass balance over the reactors given the composition, pressure, temperature and mass flow for inlet flows as well as the circulating particle flow. The model provides as result values for composition, pressure, temperature and mass flow of the outlet flows, as seen in Figure 12. In the model used, a number of assumptions have been made which are summarized in Table 2 and, in some cases, discussed further.

Table 2: Assumptions made in the CLOU ASU model

	CLOU ASU Assumptions
1	Each reactor is considered a continuously stirred tank reactor (CSTR) with perfect mixing
2	Reactors are in equilibrium
3	All gases and gas mixtures are considered ideal
4	Pressure levels are assumed constant throughout each reactor
5	Pressure difference between the reactors are set to a maximum of 0.2bar
6	There are no losses in terms of energy, pressure or mass
7	Conversion of the pure metal is assumed to be 95%

Perfect Mixing

Perfect mass and thermal mixing implies constant concentration and temperature profiles throughout the reactors. Thus, as soon as the CLOU particles enter a reactor, they attain the overall reactor temperature instantly. Also, any reduction in oxygen capturing or releasing efficiency due to fluidization issues inside the reactors is disregarded.

Reactors are in equilibrium

The influence of residence time versus the time it takes for the particles to capture or release oxygen is handled in such a way that the reactions are considered to reach the terminal composition instantly upon entering the given reactor.

Pressure Gradient within the Reactors

As oxygen is removed from, or added to, a gas stream that enters either capturer or releaser at a given pressure, the pressure inside either reactor will decrease or increase respectively. Also, fluidized bed reactors present vertical pressure gradients. It is assumed that these pressure gradients do not influence the overall assessment substantially.

Pressure Difference between the Reactors are set to a Maximum of 0.2bar

If the capturer is designed as a circulating fluidized bed and the releaser as a bubbling fluidized bed there is a possibility of maintaining a slight pressure difference between reactors which is assumed to reach no more than 0.2bar. At a lower total pressure of oxygen, the carrier particles will uncouple more oxygen at a given temperature which is desirable for the releaser [3]. Conversely, for the particles to better adsorb oxygen in the capturer, the total pressure of oxygen should be higher. Regarding the absolute pressure values (not the pressure difference between reactors), a short discussion follows.

In the capturer, as seen in Figure 8, the equilibrium concentration of O_2 for any given carrier depends on the temperature. This concentration is expressed as actual partial pressure, which means that, for the copper complexes, it is only at 1bar that the equilibrium temperature is 1029°C for an ambient concentration (21vol% or 0.21bar). At 2bar 21vol% O_2 corresponds to a partial pressure of 0.42bar and the equilibrium temperature becomes higher (roughly 1062°C). Inside the capturer a higher pressure would thereby be beneficial, as the metal complexes would be able to keep binding oxygen even at increasing temperatures (i.e. they will not stop capturing at 1029°C since the equilibrium partial pressure of oxygen is not 21% at 1029°C when the total pressure is higher than 1bar). However, the difference in pressure between the beds is assumed to be no higher than 0.2bar. If the releaser is kept at atmospheric pressure, this means that the capturer may indeed have an overpressure but the pressure must not be greater than 1.2bar in total. The equilibrium temperature for 21vol% O_2 at 1.2bar is 1038°C, which corresponds to an O_2 partial pressure of 0.252bar. The compressor work to raise the pressure of the ingoing air flow from 1bar to 1.2bar is far from negligible, and the advantages gained regarding purity and flow of the ASU must be weighed against the increased electricity demand of the system.

As for the releaser, since a high total pressure also increases the actual partial pressure of O_2, the carriers will be less prone to release the bound O_2 if the reactor is pressurized. It follows that if there is a sub-atmospheric pressure in the releaser, more O_2 could be released at a given temperature. However, decreasing the pressure inside the releaser would increase the risk of air leaking into the reactor and thereby polluting (as well as diluting) the gas mix inside it. Downstream, when the mixture enters the combustion chamber the pressure is around 1bar. This means that compression needs to take place between the releaser and the combustion chamber, should the releaser operate at sub-atmospheric pressure.

Thus, the only pressurized process setup modeled was 1.2bar in the capturer and 1bar in the releaser. Having this, the new allowed temperature intervals become wider, as seen in Figure 11. This

is beneficial since it increases the maximum allowed temperature inside and out of the capturer and thereby the amount of energy that can be supplied to the process through the air inlet. The trade-off for this increased temperature interval is the cost of compressing the air stream into the capturer.

Equilibrium curve of the copper complex
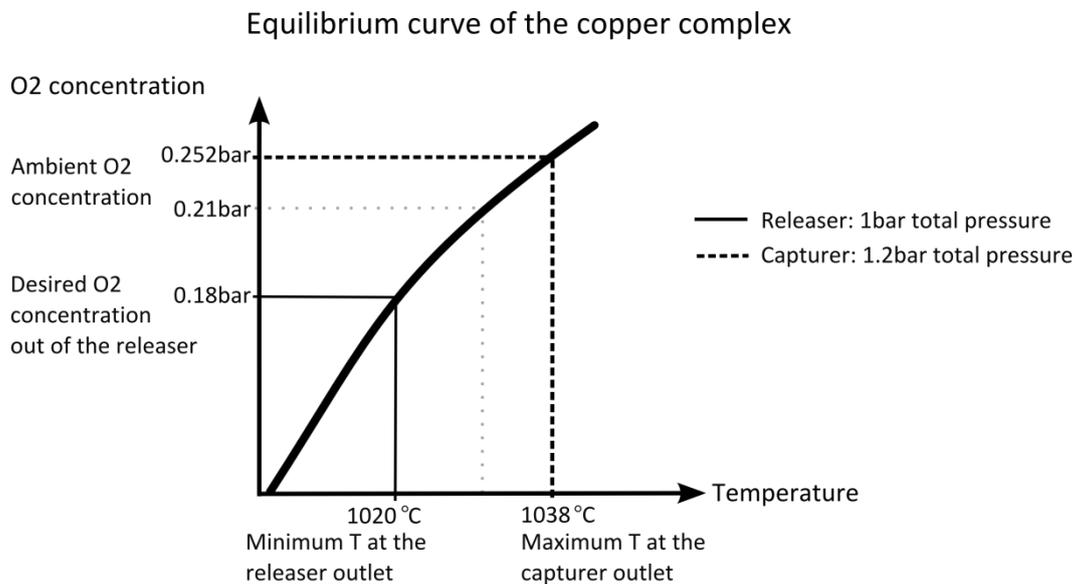
Figure 11: Equilibrium curve of CuO/Cu$_2$O with partial pressures of interest and their equivalent temperatures marked

Conversion of the Pure Metal is Assumed to be 95%

Based on experience with copper oxides it is assumed that 95% of the copper present in the system can change between its oxidized and reduced form [6]. This is assumed to be independent of the ratio between inert material and active metal. In reality this depends on the residence time, size and porosity of the particles and to some extent the inert/active ratio.

Assumptions made for the process integrations of the CLOU ASU are listed in Table 3.

Table 3: Assumptions made in order to model the process integration of the CLOU ASU

	Process integration assumptions
1	The inlet temperature of air is assumed 35°C
2	Delta T for gas/gas heat exchange is set to 20K
3	Delta T for gas/liquid heat exchange is set to 15K
4	Delta T for liquid/liquid heat exchange is set to 10K
5	For steam generation, only heat above 376°C is used
6	The flue gases are possible to cool down to 160°C (after which acid formation is assumed to take place)

CLOU ASU Model

In order to evaluate the effect of typical operation parameters presented in Table 4 on the CLOU ASU, especially their influence on the concentration of oxygen leaving the releaser, a model (see Figure 12) of the capturer and releaser was built. The model was based on a previous work

developed in Matlab by Moradell [7] and was later translated to C for use in Ebsilon Professional simulations.

Table 4: Table of ASU parameters that may be varied to obtain different oxygen concentrations

	ASU parameters
1	Type of oxygen carrier
2	Circulating flow of active metal
3	Percent active surface on the active metal
4	Type of inert support material
5	Amount of inert support material
6a	Inlet temperature into the capturer
6b	Inlet temperature into the releaser
7a	Flow of air into the capturer
7b	Flow of flue gas into the releaser
8a	Pressure inside the capturer
8b	Pressure inside the releaser
9	Composition of the flue gas into the releaser

The model solves the energy (Eq. (4)) and mass balance over the CLOU ASU in an iterative manner in order to reach a steady state solution. The CLOU ASU itself consists of one energy balance for each of the two reactors (Eq. (5) and Eq.(6)). It should be noted that additional terms, in the form of additional compounds in the inlet streams, could be added to the balance equations depending on the composition of the air and flue gas. Since the cyclic circulation of metal between the two reactors is carrying both heat and mass, each balance within the system is dependent upon the others. This fact is used to solve the overall balance for the system by making sure that the metal circulating has reached a steady state temperature. In order attain this steady state the balance for each reactor is solved separately.

$$\left(H_{N_2}\dot{n}_{N_2} + H_{O_2}\dot{n}_{O_2} + H_{CO_2}\dot{n}_{CO_2}\right)_{IN} = \left(H_{N_2}\dot{n}_{N_2} + H_{O_2}\dot{n}_{O_2} + H_{CO_2}\dot{n}_{CO_2}\right)_{OUT} \tag{4}$$

$$\left(H_{Me}\dot{n}_{Me} + H_{MeO}\dot{n}_{MeO} + H_{N_2}\dot{n}_{N_2} + H_{O_2}\dot{n}_{O_2}\right)_{IN}$$
$$= \left(H_{Me}\dot{n}_{Me} + H_{MeO}\dot{n}_{MeO} + H_{N_2}\dot{n}_{N_2} + H_{O_2}\dot{n}_{O_2}\right)_{OUT} \tag{5}$$

$$\left(H_{Me}\dot{n}_{Me} + H_{MeO}\dot{n}_{MeO} + H_{CO_2}\dot{n}_{CO_2}\right)_{IN}$$
$$= \left(H_{Me}\dot{n}_{Me} + H_{MeO}\dot{n}_{MeO} + H_{CO_2}\dot{n}_{CO_2} + H_{O_2}\dot{n}_{O_2}\right)_{OUT} \tag{6}$$

The energy balance in the two beds is solved by making sure that the energy input is equal the energy output through the use of equations for enthalpy for each compound, which gives the energy per mol at a certain temperature. For the incoming streams the molar flows and temperatures are known and thereby the energy input. For the outgoing on the other hand the equations are solved to match the energy from the incoming, giving the temperature in each bed, see Figure 12. Temperature will in turn affect the oxygen carriers equilibrium and thereby the flows of oxygen as well as reduced and oxidized metal. An initial guess of bed temperature and oxidation level of the circulating metal is made in order start the iteration loop.

C = Composition
T = Temperature
M = Mass
H = Enthalpy
H = f(C,T,M)

Values being calulated	Type of calculation executed

Input: $M_0, C_0, T_0 (H_0^{in})$

$\downarrow$

$M_1, C_1, T_1 (H_1^{out})$ — Equilibrium equation

$\downarrow$

$H_0^{in} = H_1^{out}$? — Energy balance

Yes → M_1, C_1, T_1 = output

No ↓

$H_0^{in} > H_1^{out}$?

Yes → $T_2 > T_1$ No ($H_0^{in} < H_1^{out}$) → $T_2 < T_1$

$M_2, C_2, T_2 (H_2^{out})$ — Equilibrium equation

$\downarrow$

$H_0^{in} = H_2^{out}$? — Energy balance

Yes → M_2, C_2, T_2 = output

No ↓

⋮
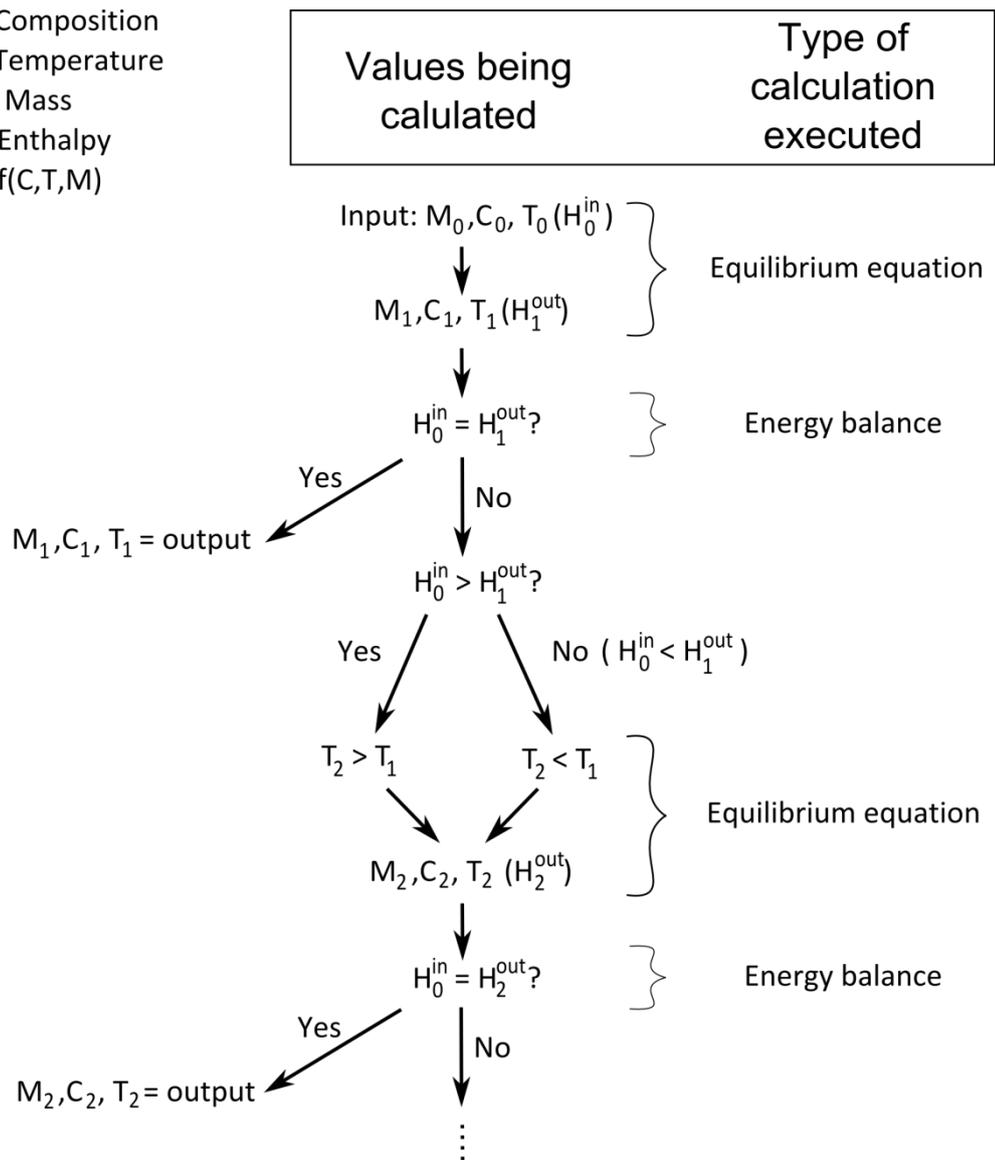
Figure 12: Schematic over the ASU models iteration process

Since a specific temperature and pressure in the reactor will correspond to a specific equilibrium partial pressure of oxygen, in accordance with the equilibrium equations (see Equations (7) to (14) based on the equilibrium curves in Figure 8), the amount of oxygen leaving the reactor can be calculated. This, due to the assumption that the gases are treated as ideal: a given partial pressure corresponds to a given concentration. When the amount of oxygen leaving the reactor is known, the amount of oxidized and reduced metal will be known, thus the mass balance over the system is solved. The mass and energy balances between the reactors are iterated. The solution is considered to be converged when the difference between the exiting temperatures of two iterations is less than 10^{-4} and the difference in mass between the entering and exiting streams is less than 10^{-4}.

Table 5: Equilibrium equations for copper

$P_{O2} = 0$	for T < 1073 K	**(7)**
$P_{O2} = 9 \cdot 10^{-88} \cdot T^{27,757}$	for 1073 K < T < 1223 K	**(8)**
$P_{O2} = 2 \cdot 10^{-12} \cdot e^{0,0195T}$	for T > 1223 K	**(9)**

Table 6: Equilibrium equations for manganese

$P_{O2} = 0$	for T < 923 K	**(10)**
$P_{O2} = 7 \cdot 10^{-71} \cdot T^{22,666}$	for 923 K < T < 1073 K	**(11)**
$P_{O2} = 2 \cdot 10^{-9} \cdot e^{0,0157T}$	for T > 1073 K	**(12)**

Table 7: Equilibrium equations for cobalt

$P_{O2} = 0$	for T < 1023 K	**(13)**
$P_{O2} = 10^{-129} \cdot T^{37,821}$	for T > 1023 K	**(14)**

A case where the two reactors are heat exchanged in order to maximize the O_2 concentration leaving the releaser was also investigated. In this case, the temperature in each bed is set to a value which gives the desired O_2 concentration in the outlet. The heating or cooling needed to achieve the desired temperature is supplied by two external heat exchanging streams, one for each reactor. Since the temperature is fixed, also the mass flow of oxidized/reduced metal and O_2 are fixed and the iterative process is instead performed to decide the size of heat exchanging streams. The temperature of the streams is calculated with the energy balance. There is also an upper and a lower minimal temperature difference defined in order to make sure that no heat is flowing from a lower temperature to a higher one.

Parameter Iteration Model

To evaluate the parameters in Table 4 (excluding the pressures, type of inert and type of active metal) and their effect on the partial pressure of O_2 leaving the releaser an iteration loop (see Appendix for figure) was created. The loop is ordered to iterate each parameter and saves the best value in regards to O_2 concentration out of the releaser. Since the optimum values of different parameters are highly dependent upon each other they cannot be iterated independently. The iterations are therefore performed with all values being varied for each loop. Because of the inter-dependence, the order in which each parameter is iterated within the loop will affect the final O_2 concentration. The order is therefore randomized. The loop initiates by assigning random, but within

set limits, values to each parameter and then varying them one by one within the limits to finally save the value that gives the highest oxygen concentration. Once a value giving the optimal concentration is found for each parameter the loop starts to iterate again with the previous optimal values, instead of the random ones, as starting guesses. This as the optimum found for every parameter is dependent on the values of the others. The loop is stopped after 20 rounds or when the convergence criteria of three identical sets of parameter values in a row occur.

Parameter Analysis

The performance of the CLOU ASU is influenced by several parameters, which may be independent or interconnected. Table 8 presents the parameters and intervals investigated in the iteration model. Certain parameters, although possible to change in principle, have been fixed at their most promising values or types to be able to focus the investigation. The parameters and their influence on the output of the CLOU ASU are discussed further in the Results section.

Table 8: Parameters and intervals investigated. Intervals are described as "start value : stepsize : end value"

	ASU parameters	Simulation interval (if applicable)
1	Type of oxygen carrier	CuO/Cu_2O
2	Amount of active metal circulating	100:100:5000 [kg/s]
3	Percent active surface on the active metal	95%
4	Type of inert support material	TiO_2
5	Amount of circulating inert support material, x	0.01:0.01:0.5 [-]
6a	Inlet temperature into the capturer	25:10:1027 [°C]
6b	Inlet temperature into the releaser	1021 [°C]
7a	Flow of air into the capturer	10:10:1000 [kg/s]
7b	Flow of flue gas into the releaser	10:10:1000 [kg/s]
8a	Pressure inside the capturer	1 [bar]
8b	Pressure inside the releaser	1 [bar]
9	Composition of the flue gas into the releaser	Pure CO_2
10	Initial temperature of particles	1027 [°C]

The amount of active metal has an effect on the amount of inert material present in the system, as it is defined as a function of the amount of active metal present; see Equation (15) and (16). The factor x is varied between 0.01 and 0.5 in the simulation, which corresponds to an inert share of maximum 99wt% of the total flow, to a minimum of 50wt% of the total flow.

$$F_{tot} = F_{active} + F_{inert} \qquad (15)$$

$$F_{inert} = (1 - x) \cdot F_{tot} \qquad (16)$$

Process Integration Model

The CLOU ASU was integrated with four systems to establish whether or not the CLOU ASU could compete with a conventional Cryo ASU, in terms of thermal efficiency. The average specific cost of oxygen production by Cryo ASU, which is the one used in the Cryo ASU reference case, is 0.4kWh/Nm³, and is expected to reach 0.3kWh/Nm³ by 2012 [5]. When comparing process integration alternatives some parameters (shown in Table 9) are fixed at beneficial values for all

cases. To reach desired oxygen concentrations in each case, the flow sizes and temperatures are varied.

Table 9: Parameters and their values which are not varied for the 4 investigated process integration setups

	Parameter	35kg/s O_2
1	Type of oxygen carrier	CuO/Cu_2O
2	Percent active surface on the active metal	95%
3	Type of inert support material	TiO_2
4	Pressure inside the releaser	1bar

The different integration designs for the CLOU ASU, together with oxy-fuel combustion and a steam turbine cycle for power production (see Figure 13), were assessed by modelling in Ebsilon Professional. First two cases with production of O_2 with a concentration of 18vol% in CO_2 are presented; one Ambient case at ambient pressure and one Compressed case with overpressure in the capturer. Case Steam assesses the production of 100vol% O_2 by condensing steam. Case HEX investigates the possibility of adding more heat to the releaser than what may be carried in the entering flue gas flow alone. None of the investigated cases, or their reference cases, includes the impact of flue gas cleaning.
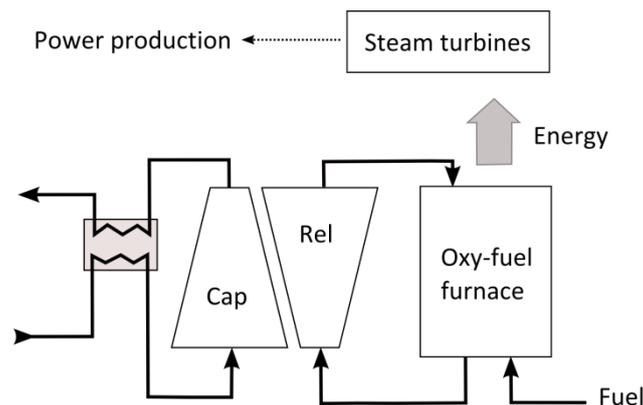
Figure 13: Basic process integration setup for the investigated CLOU ASU cases

Table 10: Summation of process integration alternatives compared

Case	Pressure inside the capturer [bar]	O_2 concentration out of the releaser [vol%]	Condensing?	O_2 production [kg/s]
Ambient	1	18	No	35
Compressed	1.2	18	No	35
Steam	1	16.5	Yes	35
HEX	1	31.8	No	76

The first three cases (Ambient, Compressed and Steam) are tuned to produce enough oxygen to correspond to a stream of 18vol% O_2 (35kg/s) and 82vol% CO_2 (219kg/s), as seen in Table 10. The HEX case produces 31.8vol% O_2 (76kg/s) in 68.2vol% CO_2 (231kg/s). The efficiencies of the four processes were assessed by comparing them to a Blank reference case which was assumed to be fed with an oxygen mix for free (i.e. produced without energy penalty), and a Cryo reference case which had its

oxygen demand covered by a Cryo ASU (see Figure 14). The efficiencies were measured as thermal efficiencies, which is the net electricity production per fuel consumption. The fuel was in all cases assumed to be pure coal with a specified net calorific value of 33924kJ/kg.

a) Blank reference case   b) Cryo reference case   c) Investigated cases (Ambient, Compressed, Steam and HEX)
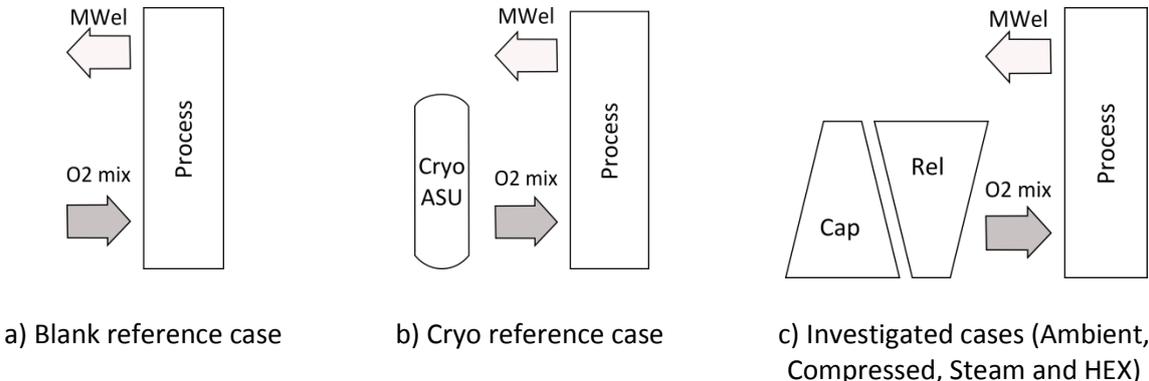
Figure 14: The difference between the references (a and b) and the investigated cases (c)

Results and Discussion

The assessment of the fluidized bed-based ASU proposed in this report is based on the understanding of the influence and inter-dependence of process parameters as well as the limitations of the process. The results are presented in two parts:

1. The influence of the parameters internal to the CLOU ASU are discussed based on parameter interval of the CLOU ASU model.
2. Possibilities for process integration of the CLOU ASU with the oxy-fuel process are assessed.

The CLOU ASU

Simulations of the CLOU ASU unit were performed regarding the influence of the parameters shown in Table 8 on partial pressure of O_2 out of the releaser. The listed parameters in Table 8 were varied within their simulation intervals. Other outputs of interest were also plotted, such as the flow of oxidized and reduced metal flowing between the capturer and releaser and the temperature inside the reactors.

For a given set of data, where only one parameter is varied, the resulting plot would display the corresponding trend. But since it is the general parameter dependence and the overall behavior of the CLOU ASU that is of interest, many sets of data are used for each varied parameter. This is seen in the plots as a number of trends which together form an overall trend. For resulting values, such as temperature inside the reactors, the plots include data from all varied parameters.

The simulation results are used to obtain an overview of the inter-dependence of the parameters which helps to understand the behavior of the capturer and releaser. In this chapter, all result figures presented show the influence of the investigated parameters on the concentration of oxygen (as partial pressure) where each node is the partial pressure of O_2 out of the releaser at a given set of parameter value combinations.

Type of Oxygen Carrier

When deciding between the three types of oxygen carriers (copper, manganese and cobalt), the availability, price, toxicity, robustness and rate of reaction must be considered. Cobalt was excluded after modeling because of its high heat of reaction and substantial increase in carrier weight per mole of oxygen transferred (combined with its specific heat capacity). Manganese is known [Mattisson et al.] to have a too low reaction rate to be of interest for chemical-looping applications. Thus, the present study is focused on the CuO/Cu_2O carrier.

Amount of Circulating Active and Inert Metal

The effect of the circulating amount of active metal on the partial pressure of O_2 out of the releaser is presented in Figure 15. The amount of active metal present in the system limits the oxygen transfer in two ways. If the equilibrium concentrations of oxygen are not reached in any of the two reactors (capturer or releaser), a limited flow of active metal is governing the performance of the CLOU ASU. On the contrary, a large metal flow inside the system represents a significant thermal inertia which is not always optimal in terms of achievable O_2 purity.
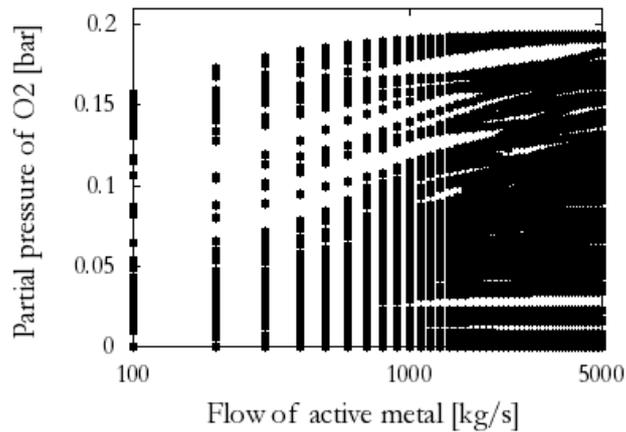
Figure 15: Partial pressure of O₂ in the flow out of the releaser at different flows of pure active metal in the ASU

As seen in Figure 15, the partial pressure of O_2 reaches high values (almost 20vol% O_2) at almost all investigated flows of active metal inside the ASU. This indicates that within the given parameter intervals the required amount of active metal needed to reach high O_2 concentration is quite low and increasing the amount has no effect, due to that thermal inertia is high enough even at low circulating flows of oxygen carrier. There is however a decline in the concentration at carrier flows below 500 kg/s indicating that either there is not enough active metal to carry oxygen between the reactors and/or that the decreased thermal inertia results in a lower temperature inside the releaser (and thereby a decreased oxygen concentration).

Support inert material is required to prevent crushing of the active material (which reduces porosity and thereby active surface, leading to reduced oxygen carrying efficiency). The inert material content also contributes to the thermal inertia of the solids circulating flow, and thus tends to decrease the temperature difference between the two reactors in the system. If a small temperature difference between the two reactors is desired, the solids flow should in general be increased, and particle structural stability, heat capacity and price will determine the optimal distribution between active and inert metal in the flow. In the model, TiO_2 was used as inert material, based on findings made by J. Adánez et al. [8]. In process integration studies shown later on, the amount of inert TiO_2 was increased when more thermal inertia was required in order to decrease the temperature difference between reactors. For iteration of the outlet concentration of O_2 however, the model found optimal mixes *completely independent* of economically reasonable flow sizes. The influence of the flow of inert material is seen in Figure 16.
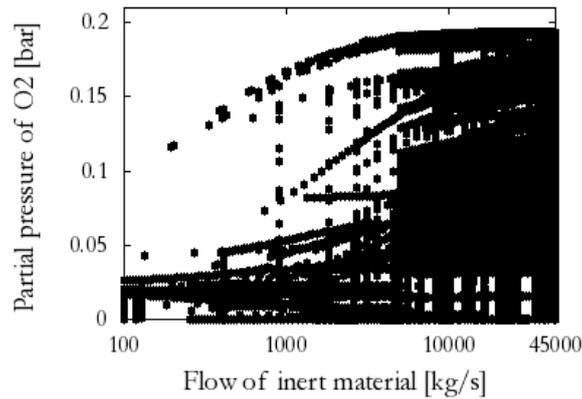
Figure 16: Partial pressure of O₂ out of the releaser at different flows of inert material

The influence of the flow of inert material on the outlet oxygen concentration is similar to that of active metal, as seen in Figure 16. The reason for this behavior is also the same as for active metal, i.e. high thermal inertia is already reached at relatively low values for the flow and an increase has no effect after this. A too low flow, as expected, gives lower oxygen concentrations probably due to the decreased thermal inertia.

Capturer Inlet Temperature
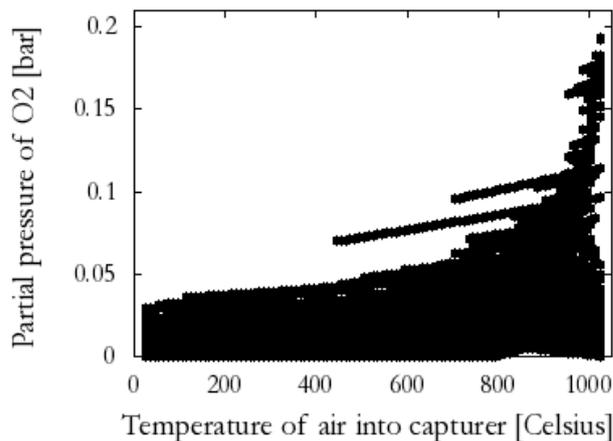
Figure 17: Partial pressure of O₂ out of the releaser at different temperatures of the air flowing into the capturer

The influence of the inlet temperature of air into the capturer on the partial pressure of O_2 out of the releaser can be seen in Figure 17. It shows that in order to get high O_2 concentrations a high temperature into the capturer is required. This since there is an enthalpy inflow requirement to reach the temperature level of the system leading to high O_2 concentrations in the releaser.

In the capturer the temperature will increase every time O_2 is captured by the active metal as the carrier oxidation is exothermic. This temperature increase is counterproductive for further capture since at higher temperatures equilibrium moves toward higher O_2 concentrations and the copper oxide particles will eventually stop capturing O_2 completely at 1029°C (where equilibrium dictates that ambient air O_2 concentration, 21vol%, prevails at a total pressure of 1bar). It follows that the air flow into the capturer needs to be cold enough to allow enough exothermal oxygen capture before temperature is increased and capture stops.
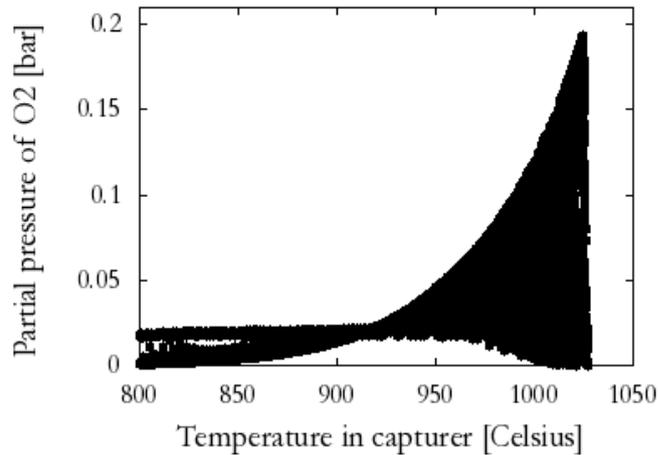
Figure 18: Partial pressure of O₂ out of the releaser at different capturer temperatures

Looking at the influence of the capturer temperature in Figure 18 it becomes clear that the highest O_2 partial pressures occur at temperatures close to the maximum allowed (1029°C). As previously mentioned, at higher temperatures the active metal would stop capturing oxygen. Above 920°C the capturer is no longer colder than the releaser and, as it instead begins to provide more heat for the releaser, helps increasing the product concentration of oxygen out of the releaser.

Releaser Inlet Temperature

With the heat balance of the reactors depending only on the ingoing flows and amount of reactions; the inlet temperature to the releaser must be high enough to cover the temperature decrease caused by the endothermic O_2 release reaction. If the temperature is allowed to drop too much, the particles will stop releasing oxygen completely. Therefore the inlet temperature of flue gas into the releaser must be high enough to cover the temperature drop of the release reactions. At 1200°C the copper particles will sinter however, so the temperature thereby has a maximum limitation.

If the metal entering the releaser is heavily cooled in the capturer, the inlet flue gas flowing into the releaser must provide even more energy to accomplish a suitable temperature for oxygen release. As may be deduced from Figure 19, the required outlet temperature of the releaser to reach a concentration of 18vol% O_2 at a total pressure of 1bar is at least 1020°C. Meanwhile, the temperature of oxygen deprived air leaving the capturer must not exceed 1029°C as that is the equilibrium temperature for an oxygen partial pressure of 21vol%, i.e. the ambient concentration. The temperature at the capturer exit must be lower than this if any O_2 is to be captured by the particles at all.

Equilibrium curve of the copper complex
at a total pressure of 1bar
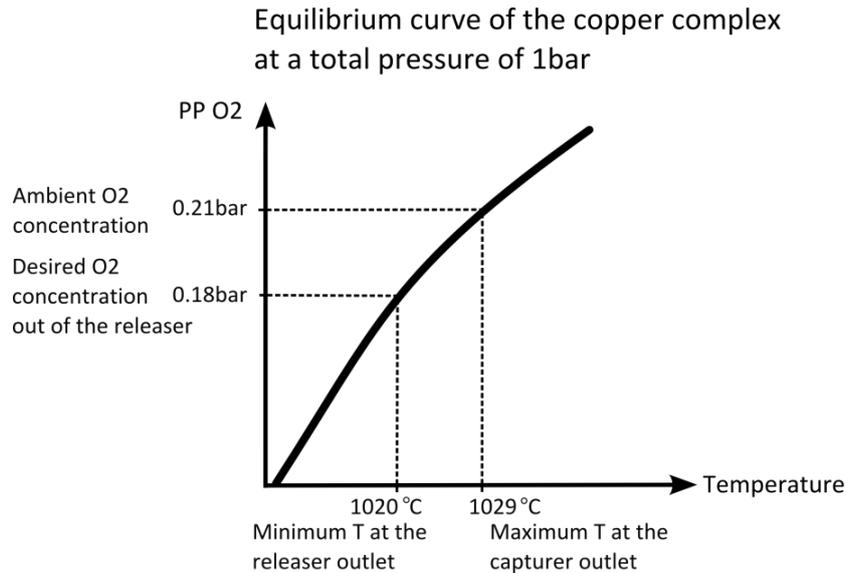
Figure 19: Equilibrium curve of CuO/Cu$_2$O at ambient total pressure
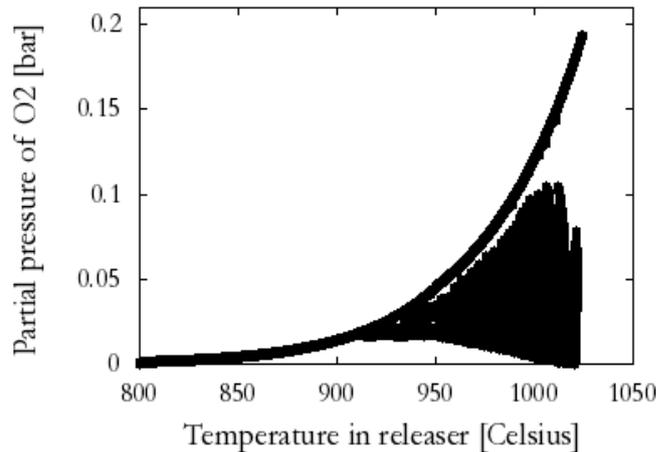
Figure 20: Partial pressure of O$_2$ out of the releaser at different temperatures inside and out of the releaser

Figure 20 shows that the outlet partial pressure of O$_2$ follows the equilibrium nicely and, as expected, increases with the temperature. In the iteration model the inlet temperature of CO$_2$ to the releaser was fixed at 1021°C for all runs.

Air Flow into the Capturer

The enthalpy flow provided to the capturer stems not only from inlet temperature but also from the magnitude of the air flow entering the capturer. The air flow is also the source of O$_2$ to the process and therefore has a limited minimum value. If the temperature increases inside the capturer, the outgoing gas flow contains more heat than the ingoing and may be used for preheating the incoming air to a reasonable extent. This air preheating is advantageous since, even if a cold environment is beneficial inside the capturer in terms of binding O$_2$, the outlet temperature must be high enough not to cool the releaser beyond its minimum temperature for 18vol% O$_2$ concentration (see Figure 19). Figure 21 shows that there is a substantial spread of eligible air flow rates into the capturer. This shows that high outlet O$_2$ concentrations can be reached with both high and low air flows for the given set of varied parameters (given in Table 8). However, a maximum temperature of the ingoing air flow was set to 1027°C to not risk cooling the capturer and, by extension, the releaser. If this

23

maximum temperature value allowed had been lower, high flows of air into the capturer would have decreased the O_2 concentration out of the releaser due to its cooling effect on the CLOU ASU system.
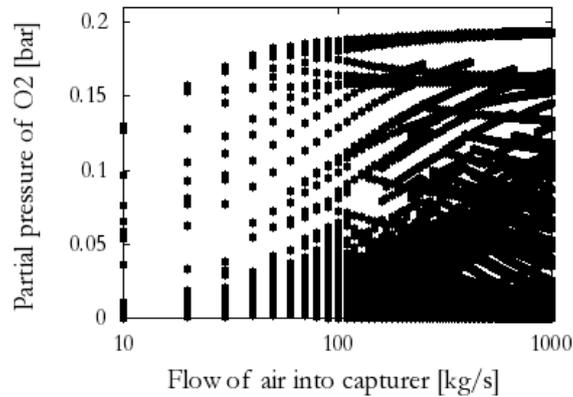
Figure 21: Partial pressure of O_2 out of the releaser at different air flows rates into the capturer

Flow of Flue Gas into the Releaser
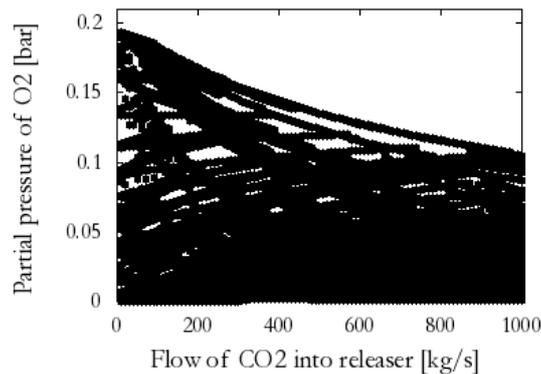
Figure 22: Partial pressure of O_2 out of the releaser at different CO_2 flow rates into the releaser

The O_2 release reaction is endothermic, and unless heat is added continuously, the equilibrium concentration of O_2 will soon decrease below what is desired out of the releaser. The heat addition comes from the circulating metal and the inlet flow of flue gas: either from their high temperature, large flow rate or both. The flow rate also influences the outlet concentration of O_2 since a large gaseous flow dilutes a given amount of O_2 released. A small flow would then, theoretically, enable a higher oxygen concentration. This is seen in Figure 22, where the outlet concentration of O_2 is higher at small CO_2 flows.

Composition of the Flue Gas into the Releaser

The flow rate and temperature of the flue gas entering the releaser will result in different enthalpy additions to the releaser depending on the composition of the flue gas. A flow of pure steam has a higher specific heat capacity than one of CO_2 or a mix of the two. The composition does not have a direct influence on the metal/oxygen equilibriums and is dependent on the proximate composition of the fuel being combusted in the furnace as well as the degree of flue gas cleaning and separation. In this report the flue gas stream is assumed to be pure CO_2 if nothing else is mentioned.

Other Effects of Parameter Variation
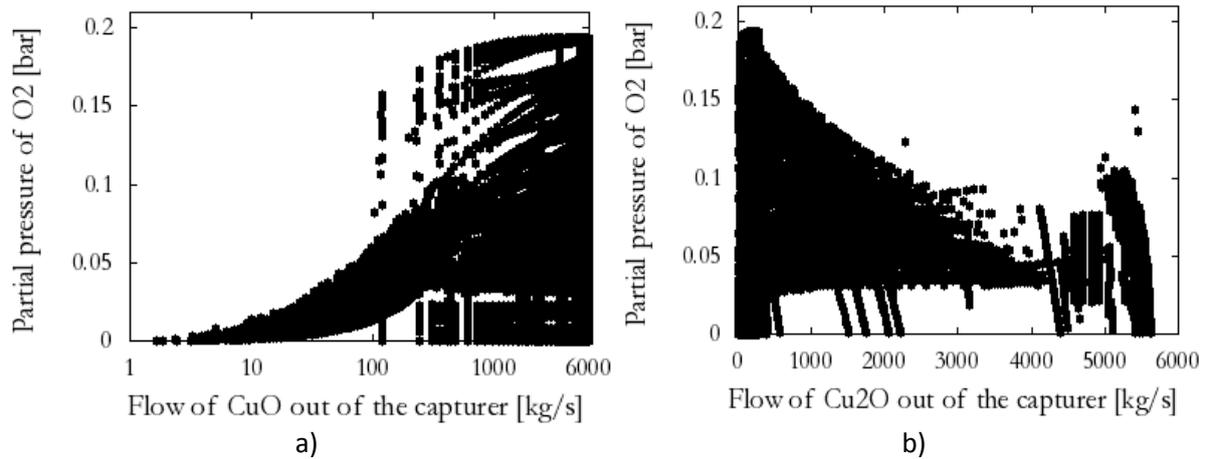
Figure 23: Partial pressure of O_2 out of the releaser at different amounts of a) oxidized metal complex leaving the capturer (logarithmic scale), and b) reduced metal complex leaving the capturer

The flows of oxidized and reduced metal leaving each reactor are not operational parameters (i.e. inputs) but resulting outputs of the model. Their correlation with the outlet oxygen concentration is seen in Figure 23 and 24. These figures depict that, in general, high partial pressures of oxygen are achieved when the amount of oxidized metal leaving the capturer is high and the amount of reduced metal is low. However, as seen in Figure 23a, high partial pressure may be achieved with a range of different amounts of oxidized metal leaving the capturer. Figure 23b on the other hand indicates that the highest O_2 concentrations are reached when the amount of reduced metal leaving the capturer is small. However, the figure also shows that it is possible obtain decent O_2 concentrations also at large amounts of reduced metal leaving the capturer.
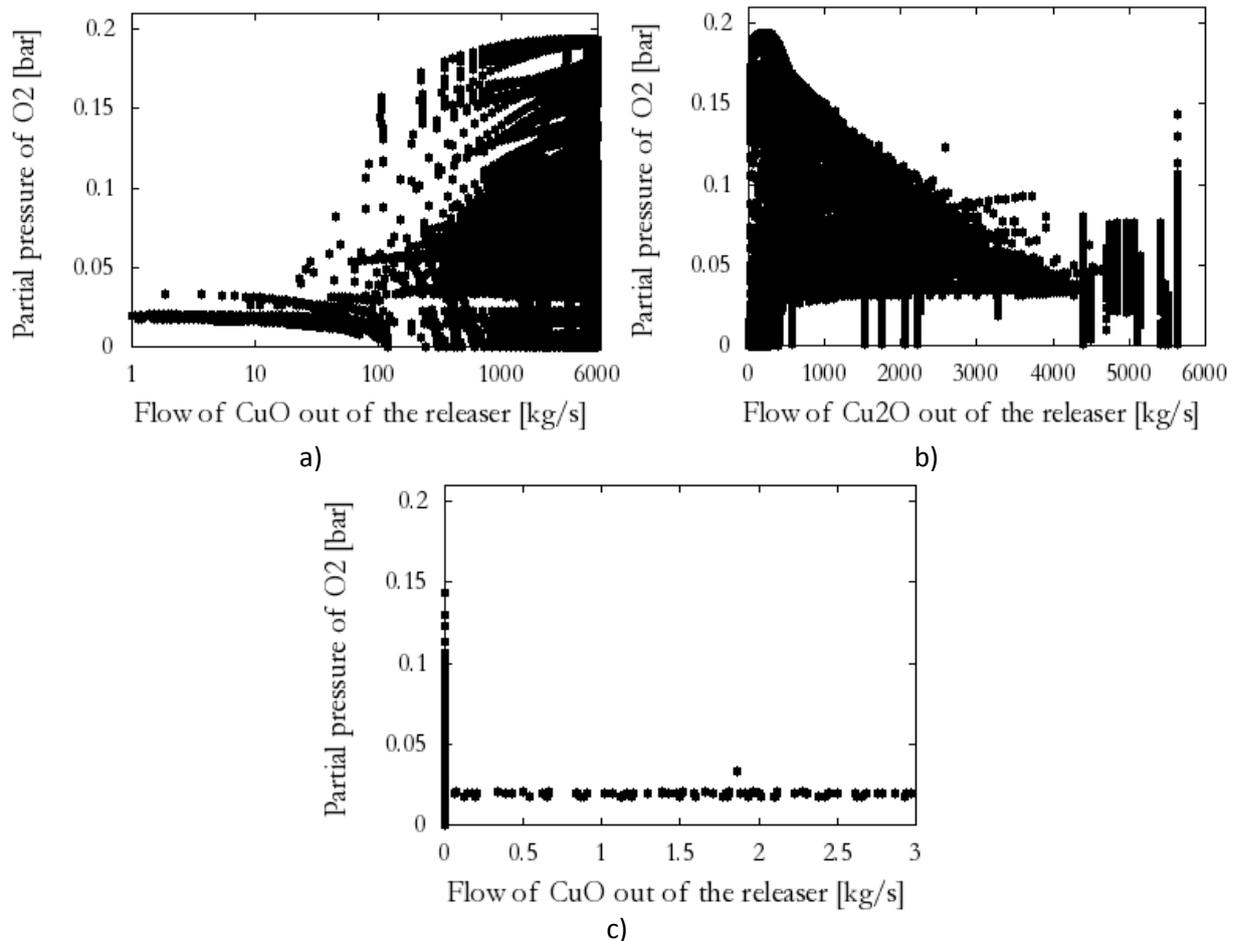
Figure 24: Partial pressure of O₂ out of the releaser at different flows of a) oxidized metal complex leaving the releaser, b) reduced metal complex leaving the releaser. c) A magnification of a) in the origin of the ordinates axis

The carrier flows leaving the releaser have a less intuitive coupling to the outlet O_2 concentration. In fact, Figure 24a shows that in general a lot of the metal oxide complexes may remain oxidized even upon leaving the releaser if high partial pressures of O_2 are to be obtained. Figure 24b is in accordance with this, as it implies that the flows of reduced complexes should be small to reach high partial pressures of O_2. The figure also shows that it is possible obtain decent O_2 concentrations also at large amounts of reduced metal leaving the releaser. Also, as seen in Figure 23a, at very low amounts of CuO leaving the capturer, the resulting partial pressure of oxygen leaving the releaser is less than 2%. These nodes correspond to the low (less than 2%) oxygen partial pressures at zero CuO flow out of the releaser seen in Figure 24c.

A Summation of the Limitations Regarding the CLOU ASU

There are a number of conditions that limit the performance of the process, the majority of which are based on the carriers and their properties. A summation of the CLOU ASU limitations is presented in Table 11.

Table 11: Limitations connected to the ASU

	CLOU ASU limitations
1	Equilibrium curve of the carrier
2	Carrier sensitivity to temperature
3a	Exothermic reaction in the capturer
3b	Endothermic reaction in the releaser

Different carriers require different temperatures to reach a given equilibrium concentration of oxygen around them (see Figure 8). All three carriers studied (copper, cobalt and manganese), require temperatures above 750°C to start the capture/release of oxygen, and temperatures around 1000°C to reach O_2 concentrations of interest for the power industry. This, combined with material limitations of different kinds, limits the possibility of process integration. If a material was found with an equilibrium curve at much lower temperatures (ideally below some 350°C as at temperatures above this the flows may be used for steam generation and heating in steam turbine power plants), process integration and thereby economy would greatly improve. Lower working temperatures might also enable external heat exchanging of the reactors, which would enable production of O_2 at higher concentrations out of the releaser. This, since the rate and temperature of the inlet flows could be fitted to the process independently of the heating demand of the releaser and the cooling demand of the capturer.

Steel equipment is considered to be able to handle temperatures up to about 600°C [9], but more expensive materials can be used at higher temperatures [10]. The investment cost depends, in part, on the material required for the reactors and piping, and even though such costs are not assessed in this report they are an important part of the overall attractiveness of the CLOU ASU process.

Investigated system setups

Case Ambient: Production of 18vol% O_2 at 1 bar in Releaser and Capturer
Theoretically, the same concentration of O_2 as that inside the capturer could be achieved in the releaser without additional heat. In practice however, without providing and/or extracting additional heat from the reactors only an oxygen concentration somewhat below that of ambient air is achievable in the releaser, since unreasonably large flows of air and circulating metal would otherwise be required. This option, where the O_2 concentration in CO_2 is set to 18vol% out of the releaser, is evaluated in the present section.
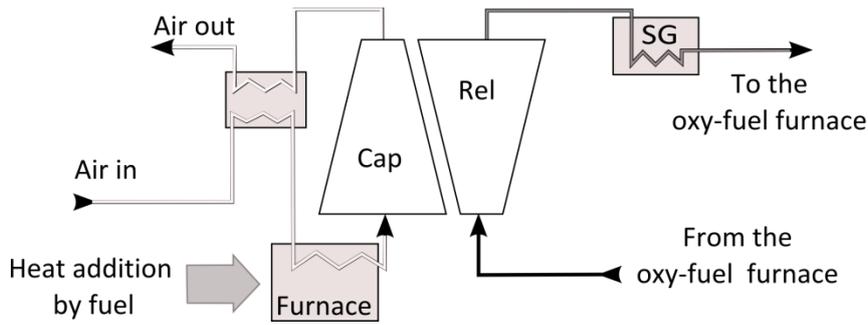
Figure 25: Process scheme with integrated CLOU ASU producing 18vol% O_2 at 1 bar

Figure 25 displays the Ambient CLOU ASU case setup. The air entering the capturer must be preheated through heat exchange with outlet oxygen-depleted air (without this, the resulting temperature of the inlet air will be insufficient to support the process with the energy required in the releaser). In the Ambient case, the inlet air flow is heated from 993°C to 1021°C through an auxiliary furnace. Flue gas is bled from the oxy-fuel furnace at a temperature of 1050°C, at which it enters the releaser. The O_2 mix exits the releaser at a temperature of 1020°C, and is cooled down to 376°C by generating steam for the power production process.
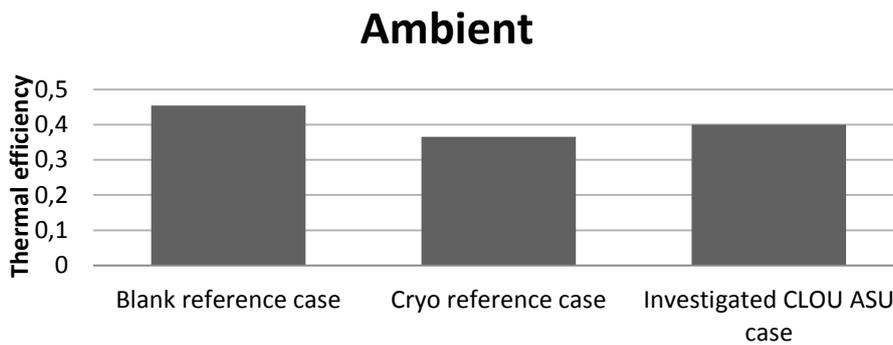
Figure 26: Thermal efficiency for the Ambient case and its reference cases

The main difference from the Blank reference case is the required heat addition to the air, but also the opportunity for steam generation by the cooling of the O_2 mix exiting the releaser. As Figure 26 shows, the Blank reference, with the same O_2 consumption in furnace as the Ambient case presented here, has a thermal efficiency of 45.4%. The Cryo reference case, with an attached Cryo ASU for O_2 mix production, consumes some of the electricity produced and therefore has a lower thermal efficiency of 36.6%. The Ambient case has a thermal efficiency of 40.0%. It should be noted that many of the heat exchange operations taking place in this model occur at high temperatures and with gas on both sides, i.e. requiring very large heat exchanging surfaces in practice.

Case Compressed: Production of 18vol% O_2 with Pressurized Capturer (1.2bar)

It is possible to, without adding heat to the releaser, reach higher concentrations out of the releaser than 18vol%, if the pressure inside the capturer is increased by compressing the incoming flow of air. This is possible since the maximum allowed equilibrium temperature inside the capturer is then increased and more heat can be transferred between capturer and releaser. Thereby higher temperatures may be reached inside the releaser which in turn enables higher outlet concentrations of oxygen than the ambient 21vol%. A pressure difference between the capturer and the releaser implies that a certain temperature difference between those two larger than that for the Ambient

case can be accepted , and thus the required thermal inertia provided by circulating metal is reduced. As the allowed increase in temperature inside the capturer is less strict, the flow of air may also be reduced. To compare the additional power consumption of the required compressor with the gain presented by the reduction of flow sizes, the outlet concentration of oxygen was set at 18vol% so as to facilitate comparison of the results with the Ambient case.
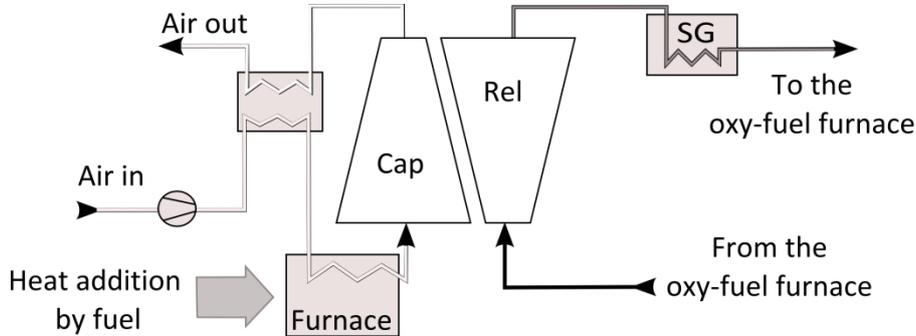
Figure 27: Process scheme for integrated CLOU ASU which produces 18vol% O_2 at 1.2bar in the capturer and 1bar in the releaser

Figure 27 displays the Compressed CLOU ASU case setup. Here the air is initially compressed to 1.2bar, an operation which increases the temperature to about 55°C, up from the inlet temperature of 35°C. Due to this, the outgoing air stream cannot go below 75°C, as the lower terminal temperature difference is set to 20K for gas/gas heat exchange. The furnace heats the ingoing air flow between 983°C and 1023°C. As in the ambient case, flue gas (CO_2) is bled from the furnace and enters the releaser at 1050°C. The outlet from the releaser is cooled by steam generation down to 376°C before entering the furnace at an O_2 concentration of 18vol%.

With the target outlet concentration of O_2 out of the releaser set to 18vol%, the benefits of increased pressure inside the capturer consist of the reduction in required air flow rates and of circulating metal. However, the flow of air into the capturer required is still considerably larger than the flow of flue gas entering the releaser. This since the temperature at which the capturer operates will only support a small decrease in oxygen concentration from the ambient of 21vol% and as the corresponding increase in concentration in the flue gas stream is considerably greater (0vol% to 18vol%) there would simply not be enough O_2 transferred between the beds if the flows were of the same magnitude. The power required to compress this large flow of air to 1.2bar is substantial.
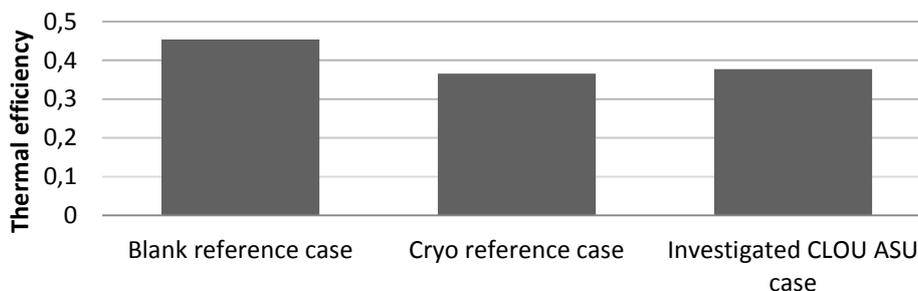
Figure 28: Thermal efficiency for the Compressed case and its reference cases

Looking at Figure 28 and bearing the results of the Ambient case in mind (Figure 26), it seems that the benefits that arise from keeping a pressure difference between the capturer and the releaser are not significant enough to justify the required compressor work. The thermal efficiency in the compressed case is 37.7% while the Blank reference case has 45.4% with the same O_2 consumption. The Cryo reference case has a thermal efficiency of 36.6%. It should be noted again that many of the heat exchange operations in this arrangement occur at high temperatures and have gas on both sides, leading to the need of extremely large heat exchanging surfaces.

Case Steam: Production of 100vol% O₂ by Condensing Steam

By using steam instead of CO_2 as the gas stream entering the releaser, the actual outlet concentration becomes less important since steam may be condensed to create a stream of pure O_2. This separation is less demanding than separating O_2 from N_2 or CO_2 as it occurs at 100°C at ambient pressure.
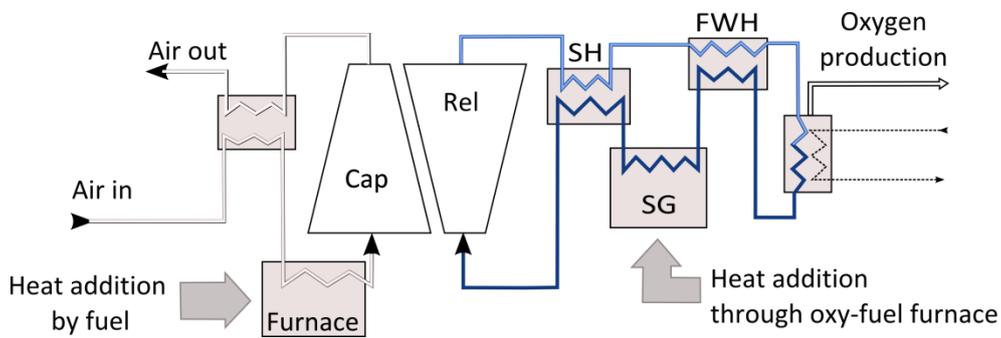
Figure 29: Process scheme for integrated CLOU ASU producing 100vol% at 1bar in capturer and releaser while using steam as inlet gas in the releaser

The Steam case then has a product like that of Cryo ASU: next-to-pure oxygen. The inlet air requires heating in an auxiliary furnace from 996°C to 1020°C, and the steam entering the releaser has a temperature of 990°C at 1bar. As the steam exiting the releaser is at a temperature of 1016°C it requires a substantial amount of cooling to go down to 100°C for condensation. This heat is used to reheat the condensed water and super heat the re-generated steam. The actual steam generation however, requires further addition of energy. As may be seen in Figure 29 there is a possibility of district heating in the condenser, which could possibly offset some of the extra energy requirement for steam generation.
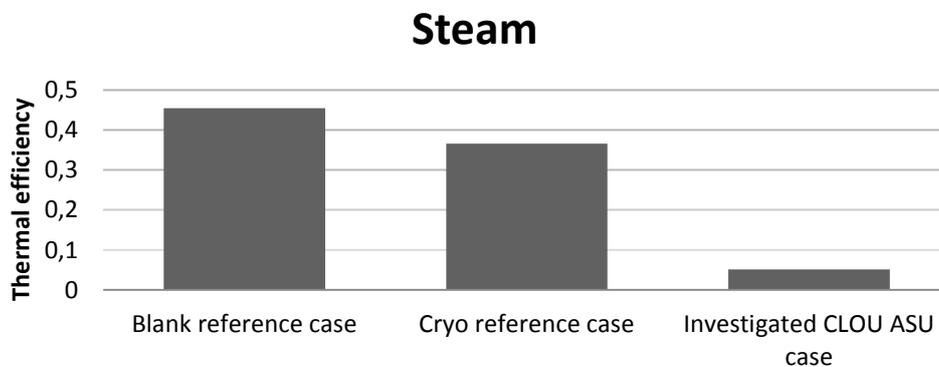
Figure 30: Thermal efficiency for the Steam case and its reference cases

However, Figure 30 shows that this potential source of income is not enough to justify the Steam case setup for power production. Using the same oxygen consumption, the Blank reference has a thermal efficiency of 45.5%, the Cryo reference 36.6% and the Steam case has a thermal efficiency of only 5.1%. It should be noted that, once again, many of the heat exchange operations in this model takes place at high temperatures and with gas on both sides. Also, since the pressure inside the releaser should not exceed 1bar, the steam entering the releaser must be at the required 990°C at 1bar.

Case HEX: Production of 31.8vol% O$_2$ with Heat Exchanged Capturer and Releaser

By heating the releaser the achievable equilibrium concentrations of oxygen in the outlet stream are increased. Cooling the capturer increases the amount of O$_2$ that can be captured at any given flow. Performing these two heat exchange operations thereby enables production of 31.8vol% O$_2$ at moderate flows of air through the capturer.
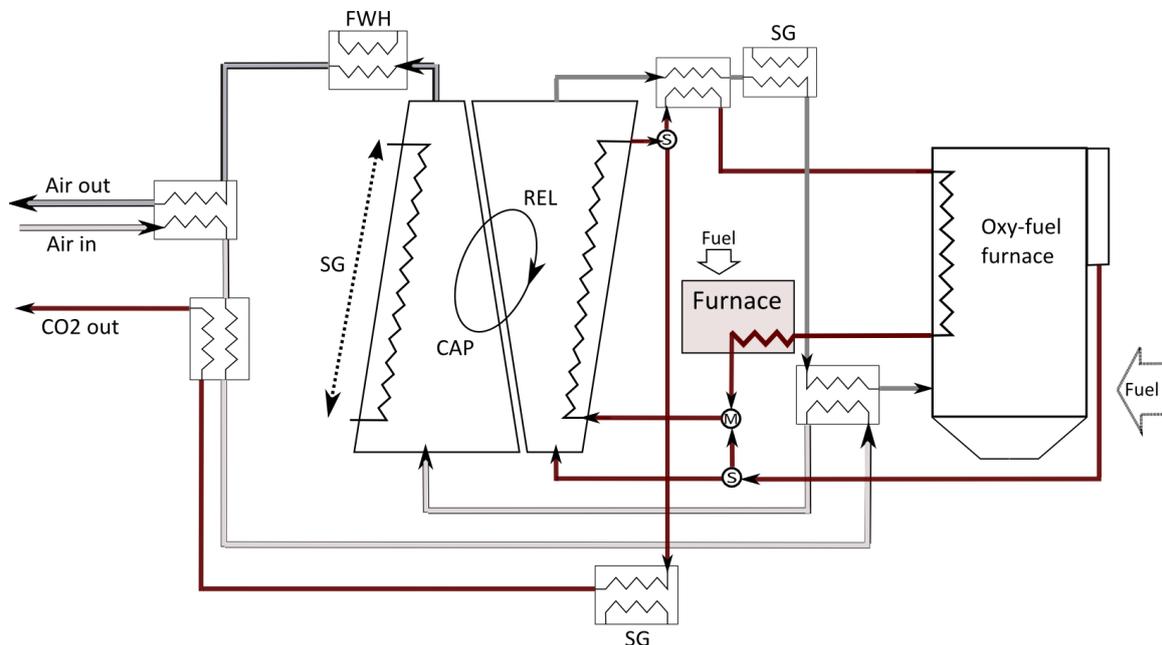
Figure 31: Process scheme for integrated CLOU ASU producing 31.8vol% at 1bar in capturer and releaser with heating of the releaser and cooling of the capturer by external streams

Figure 31 displays the HEX CLOU ASU setup. The incoming air flow is preheated in several steps before entering the capturer at a temperature of 312°C. Even though the capturer is actively cooled by generating steam for the power production process, the outlet temperature of the capturer is still high; 890°C which corresponds to an equilibrium oxygen concentration in the outgoing air of 1.6%. The CO$_2$ enters the releaser at 1000°C and exits at 1050°C. The circuit which heats the releaser is, in the model, also set to be CO$_2$ which is reheated mainly in the furnace. To avoid accumulation a split is placed just after the releaser and the heat still available (the circuit stream is 950°C at this point) is recovered by steam generation and preheating of air. The 31.8vol% oxygen mix exiting the releaser is cooled down to 376°C by reheating the heating circuit and generating steam for the power production process, before entering the furnace.

In this HEX case, the entire furnace output is required to reheat the heating circuit, but even then the oxygen produced in the CLOU ASU is not enough for the CO$_2$ in the heating circuit to reach the target

1200°C, a temperature required to heat the releaser. The final 23K (to compensate for the somewhat colder stream from the oxy-fuel furnace being mixed in) must be supplied by additional firing, which is assumed to operate on air in this model. This additional air stream (70kg/s) is preheated as well, by outgoing streams and the flue gases produced in the furnace for additional firing for increased overall efficiency.
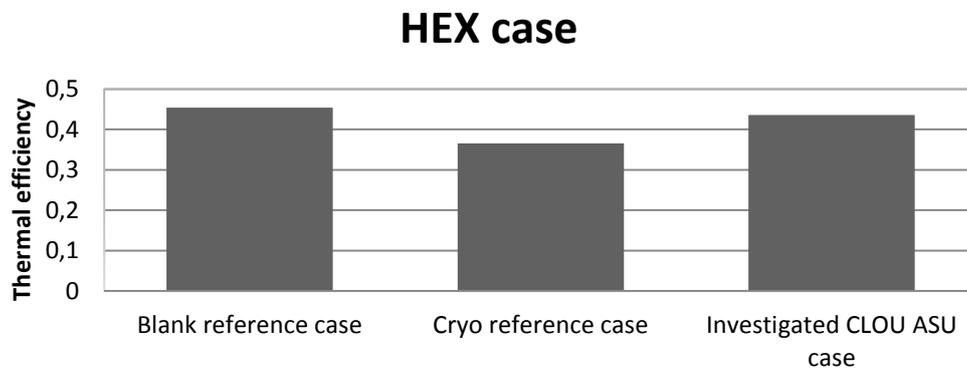
HEX case

Figure 32: Thermal efficiency for the HEX case and its references

The opportunity to recover the majority of the heat explains the thermal efficiency of the HEX case displayed in Figure 32. The extent of the possible heat recovery is due to the ability of air streams to be cooled further than flue gas streams without encountering precipitation problems etc. It should be noted that most of the heat exchange operations in this model are not only taking place at high temperatures and with gas on both sides, but for the heating circuit it takes up the entire heating capacity of the furnace, i.e. unrealistic heat exchange areas are required. In terms of efficiency this only has a minor impact, but the above-mentioned need to cool the furnace solely with hot flue gases (the circuit stream enters the furnace at 957°C and exits at 1183°C) has a major impact on the validity of the model.

Summation and Comparison of the Different Process Integration Setups
To compare the output of the different process setups a summation of their respective input values and efficiencies is presented.

Table 12: Summation of data for different process integration setups

Case	Air flow [kg/s]	ΔT of air in the furnace [K]	FG type	FG T when entering the releaser [°C]	Active metal [kg/s]	Inert [kg/s]
Ambient	2 000	28	CO_2	1 050	300	65 000
Compressed	1 000	40	CO_2	1 050	300	28 000
Steam	5 000	24	H_2O	990	300	100 000
HEX	350+70	N/A	CO_2	1 000	639	639

The different flows and temperatures are summarized in Table 12. In the HEX case there are two inlets of air; one for the capturer (350kg/s) and one for the additional firing (70kg/s) to heat the circuit the last 23K. None of these two streams require heating inside a furnace but are only

preheated with other gaseous streams. The Compressed case cannot recover as much heat as the Ambient case due to the compressor heating the inlet air stream somewhat. The Steam case works at a lower inlet temperature into the releaser as it does not have to achieve 18vol% concentration of oxygen at this point, but will reach 100vol% O_2 concentration after condensing of the steam. This pure oxygen stream is later diluted with CO_2 and reheated as far as possible by the outgoing flue gas stream. The oxygen mix then reaches 281°C as the exiting flue gas is cooled from 376°C to 160°C (which is considered the minimum temperature before formation of acids etc).

Thermal efficiency
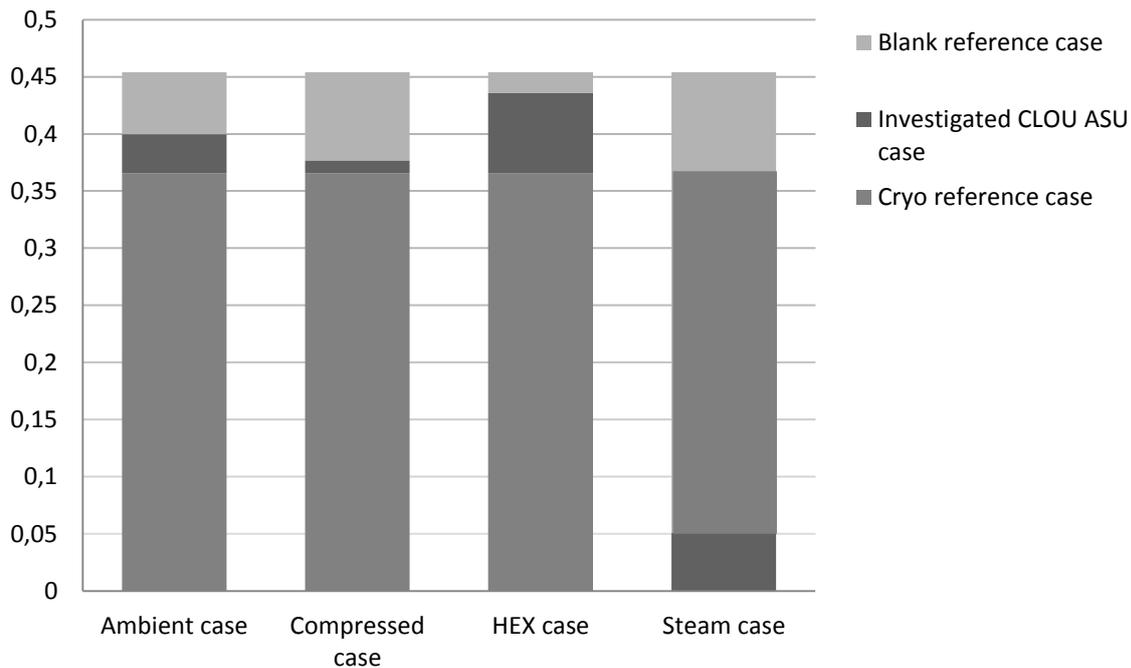
Figure 33: Lumped together thermal efficiencies of the four cases (Ambient, Compressed, HEX and Steam) and their respective reference cases

Figure 33 compares the relative thermal efficiencies of the four investigated cases. The Blank reference case, without energy penalty to produce the oxygen it uses, has the highest efficiency in all setups. In the Ambient, Compressed and HEX case, the CLOU ASU causes a smaller penalty than the Cryo ASU, even though the difference between the two O_2 separation technologies is rather small in the Compressed case. In the Steam case the Cryo reference has a thermal efficiency of 36.6%. The CLOU ASU on the other hand, has an efficiency of just above 5.1%, which proves that even if district heating is applied at the condensation of the steam, the process is not efficient enough to even come close to a process utilizing a Cryo ASU instead.

As previously mentioned, the other three cases (Ambient, Compressed and HEX) all point at the same effect: CLOU ASU causes a smaller loss of production than the conventional technique of Cryo ASU for these setups. In particular, the HEX case suffers only a very small penalty of creating the O_2 mix through CLOU ASU compared to the Blank reference case.

The main weight of the particles is made up of inert support material since the cost of the support material is less than for the active metal, tough if that is not the case it would be preferable to use

the active metal due to its higher heat capacity which would result in a smaller flow. To decide which is the optimal inert/active ratio, the cost of additional active metal needs to be compared to the cost of the increased size of the unit for the larger flow. It should also be noted that the feasibility of circulating solids flows of the magnitudes obtained has not been assessed in this work.

Limitations Regarding the Process Integration

Some limitations emerge as the system is put together. For instance, the inherent interaction between the two fluidized beds creates limitations in the system, especially when combined with the sensitivity of the equilibrium presented by the oxygen carrier.

Another example is heat recovery, which improves thermal efficiency when implemented but has a limited feasibility, since heat exchanging areas required for preheating the air going into the capturer will be substantial (due to the large flow rates, small temperature differences and low heat transfer coefficients of the gases). The high temperature levels at which heat exchange takes place also require expensive steel alloys capable of withstanding such conditions. The cost for such heat exchangers has not been assessed in this work but would increase the cost of the CLOU ASU substantially.

The fact that the combustion chamber in the HEX case is cooled down to 1000°C by circulating flue gas being heated from 957°C to 1183°C is also a severe difficulty. Again, the same obstacles cited above for air preheating apply here: large flow rates, small temperature differences and gas/gas heat exchanging, resulting in tremendous heat exchanging areas. The consequences of this are however much bigger since the amount of heat transferred is considerably higher and high temperature resistant steel alloy as construction material is required.

For the steam case, the required inlet temperature of the steam, 990°C at 1bar, is very hard to generate.

Conclusions

The possibility of separating oxygen from air by means of circulating oxidizing and reducing metal between two fluidized beds has been investigated. The drop in thermal efficiency of a power plant with such a CLOU ASU process is compared to that of a power plant with a conventional cryogenic ASU supplying the required oxygen.

The results show that the performance of a CLOU ASU is highly dependent on the amount of energy supplied to the process. As the process temperature ranges between 800-1200°C, temperature of the supplied heat must be higher than these levels. Thus, a great limitation is that piping material, suitable fluids and carrier material must be able to handle such high temperatures. Heat supply by means of flame combustion inside the reactors will dilute and contaminate the outlet stream with flue gases and is therefore not recommended.

If both the capturer and the releaser operate at ambient pressure and without external heat supply or removal, the theoretical maximum O_2 concentration in the outlet of the releaser is 21vol%. An increased pressure in the capturer could achieve higher concentrations of O_2.

Three possible process integrations to an oxy-fuel power plant have been proposed which have a lower efficiency penalty than a corresponding cryogenic oxygen production. However, there are severe practical difficulties to overcome in its implementation: heat exchanging areas required will be substantial. A compression of the air flow is not thermodynamically favorable, but the compression might however be beneficial, as it decrease the size of the air inlet and circulating particle flows and, thus, the cost of the ASU.

Future work

As this work is merely an assessment of the CLOU ASU, many areas are only briefly investigated and complements are required to provide the full picture on the feasibility of the air separation unit and its process integration options.

The validity of assumptions made should be assessed, alongside economical considerations. The technical possibility of supplying heat through direct or indirect heat exchanging drastically changes the prerequisites for the CLOU ASU process. If indirect heat exchange of the CLOU ASU was found possible to apply, the extent to which the CLOU ASU may be completely integrated into mainly an oxy-fuel combustion power plant should be further investigated.

The CLOU ASU technology is however not only limited to the oxy-fuel process, but could be used together with other CCS technologies as well as with other separation processes. One approach would be to use the CLOU ASU together with the Cryo ASU process currently established. Theoretically, if a stream with 10vol% O_2 could be produced with the CLOU ASU the required production from the Cryo ASU could be reduced by one third (given that a 30vol% O_2 concentration is desired). This should increase the efficiency for the oxy-fuel combustion process seeing as CLOU ASU seems to give less of a penalty compared to the Cryo ASU for the same amount of oxygen produced. The benefits of this combination of air separation units should be further investigated.

Pre-Separation of Oxygen for Other Separation Processes

The cryogenic ASU separates nitrogen and oxygen through distillation at temperatures below -150°C. If nitrogen is replaced with a gas with a higher condensation temperature, the distillation temperature could be increased. The concept for this setup is similar to the case with steam being the carrier gas, however, if a gas that boils below ambient temperature is used, no heat is required for vaporization. A logical choice for carrier gas is CO_2 which is available from the oxy-fuel combustion process. Theoretically, CO_2 can be delivered at the high temperatures needed (about 1000°C) and the gas is in any case supposed to be cooled to ambient temperature before storage. CO_2 also has a favorable boiling point (-57°C at 5.2bar), even though it requires a pressure of at least 5.2bar to liquify. At lower pressures CO_2 will desublimate instead of condense, which could complicate the separation process.

The cryogenic process is not the only viable option for the separation of CO_2 and O_2; other possibilities are the use of membranes [11] [12] [13] or pressure/temperature swing adsorption techniques [11] [14] [15]. Membrane separation has been suggested for both pre- and post–combustion separation, between O_2/N_2 and CO_2/N_2 respectively. However, there are problems with both methods, for separation of O_2/N_2 the problem is selectivity, leading to low purities, and for separation of CO_2/N_2 the high purity requirements of CO_2 for CCS is an issue. If a pre-separation with CLOU ASU were to be used, none of these issues would pose the same problem. Firstly, a CO_2/O_2 stream would probably not create the same selectivity issues as for O_2/N_2 [16], based on that this is not a major issue for the CO_2/N_2 separation required in post-combustion separation. Secondly, because the purity requirements for such a stream would not be the same as for any of the two former cases due to the fact that an oxygen concentration of only 30vol% is suitable for oxy-fuel combustion. Pressure/temperature swing adsorption is used for the same applications as the membrane technology and could be used for the separation, though according to [17] membrane separation is preferable at lower purity requirements which is the case for the CO_2/O_2 stream.

Currently no cryogenic facility separating CO_2 and O_2 exists. Thus, no hints about the optimal O_2 concentration in such a mix out of the CLOU ASU are available. From a Cryo ASU point of view the concentration should be as high as possible, which would lead to smaller flows, which in turn would decrease the size of the unit, and thereby its capital cost as well as the compression work. The extra cost of producing a stream with relatively high oxygen concentration from the CLOU ASU should be compared to the cost of a building and running a larger Cryo ASU, in order to see which the optimal O_2 concentration from the CLOU ASU is. The same argument is valid also for membrane and pressure/temperature swing adsorption: lower O_2 concentrations from the CLOU ASU leads to the need for larger units for the other separation techniques. Further assessment of the benefits and possibilities of separating CO_2/O_2 with the mentioned technologies needs to be made in order to see if a combination of the processes is advantageous.

Standalone O_2 production for IGCC

Another upcoming technology for CO_2 sequestration is integrated gasification combined cycle (IGCC) together with a water shift reactor which results in burnable hydrogen gas and CO_2 [2]. In order to get a pure CO_2/H_2 stream, the gasification is done with a mixture of steam and oxygen, and this stream could potentially come from the CLOU ASU.

There are different types of gasifiers where, for implementation of a CLOU ASU, the fluidized bed is the only viable option. This since the others require O_2 concentrations in the vicinity of 50vol% or even more (depending on fuel source), in order to reach the high temperatures needed for gasification [18]. The fluidized bed is on the other hand operated at lower temperatures and with much lower concentrations of oxygen, approximately 25-35vol%, in the inlet flow [19]. Oxygen concentrations of this magnitude are still hard to reach with the current CLOU ASU setups, but if the steam required for the water shift reactor, in which steam is used to convert CO to CO_2 and H_2, is introduced directly into the gasifier these could be lowered. However, this increase will lead to a lowering of the temperature in the gasifier, due to the need to heat a larger flow, which would increase the need for oxygen in order to counteract this effect.

The O_2 volume fraction in the inlet gas flow of the fluidized bed gasifier (with the steam for the water shift reactor included)is plotted against the moisture weight fraction and rank R value of the fuel in Figure 34. The rank value, R, is defined as the weight of fixed carbon in the fuel divided by the total weight of combustibles. It should be noted that the model used to obtain the data in Figure 34 is very simplified (details are given in Appendix). It is seen in Figure 34 that the required amount of O_2 increases as the moisture content of the fuel increases. This is due to the large amounts of water to be evaporated (for which the considerable amounts of energy required are supplied by combustion with oxygen). At low values of R, which implies low fixed carbon content, the oxygen need becomes very high even at low moisture fractions. The reason for this is that all the fixed carbon is combusted together with oxygen and no carbon is left to react with steam to form CO and H_2. The fact that no steam/carbon reaction is taking place will lead to a lower need for steam into the gasifier.
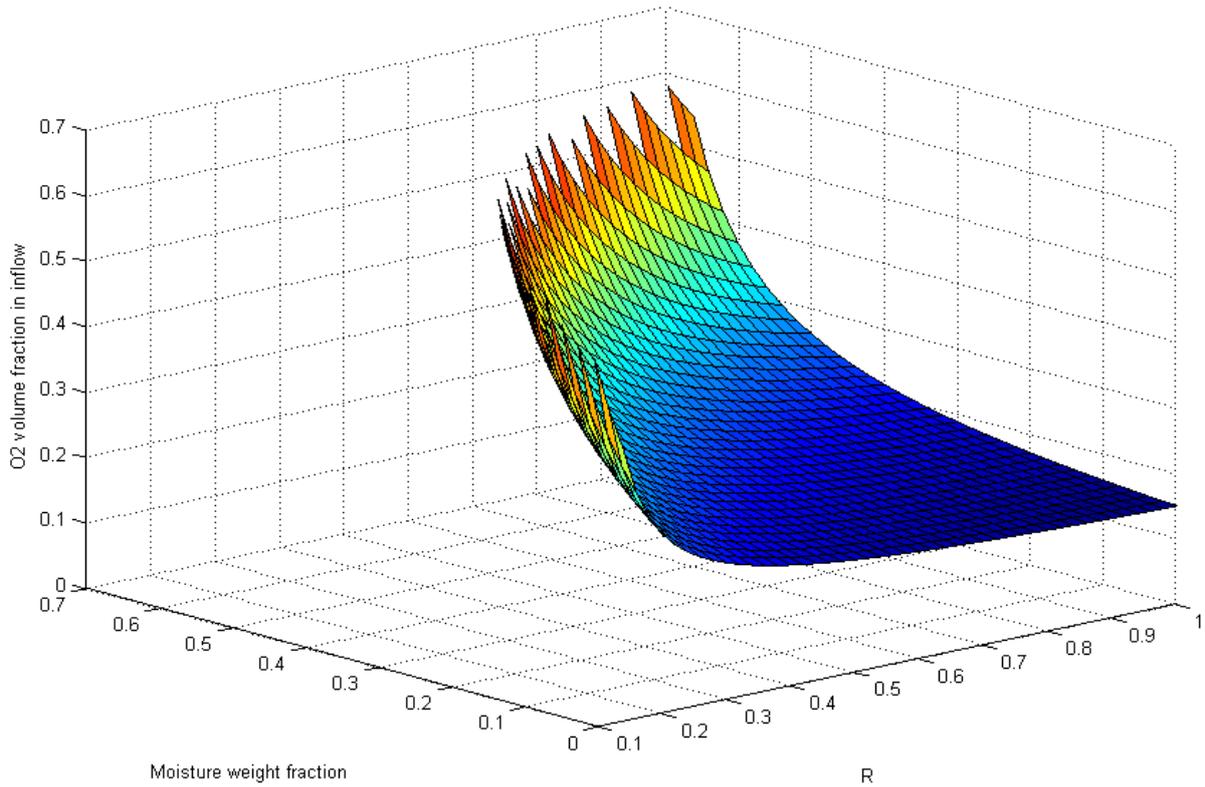
Figure 34: The oxygen volume fraction in the inlet gas of a fluidized bed gasifier of an IGCC process plotted against moisture fraction and R value of the fuel (for model see Appendix)

The ideal fuel (if the inlet flow is to be supplied by a CLOU ASU) would be a low moisture, high fixed carbon fuel. For such a case an O_2 concentration as low as 15vol% would be enough to enter the fluidized bed gasifier.

In Table 13 the composition for three different fuels that are used for gasification is shown. It can be seen that the biofuels (swichgrass and wood chips) have a low R value, leading to a need for a high oxygen concentration thus making them a bad choice for gasification together with a CLOU ASU. The composition of the coal alternative is better suited for a lower O_2 concentration, and coal is thereby a better choice for combination with CLOU ASU. .

Table 13: Composition of 3 different gasification fuels

Composition	Swichgrass [20]	Coal [18]	Wood chips [21]
Moisture weight fraction	0.20	0.111	0.064
R	0.226	0.558	0.187

Acknowledgements

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Appendix

Create a set of input values (within predtermined intervals) at random, which will work as start values for the iteration

Randomize the order in which the iteration loops will be run

Loop: Iterate over the interval of A and save the best value for pO2

Print the value for each parameter and resulting value to file for plotting

Loop: Iterate over the interval of B and save the best value for pO2

Print the value for each parameter and resulting value to file for plotting

Run through loop A + B + ... in the same order as they were just run, continuously saving the best values for each parameter in terms of pO2 20 times or until they converge and stabilize

Figure 35: Iteration design

Energy balance for IGCC gasification

In order to estimate the oxygen concentration need for a fluidized bed direct gasifier process a simple model was used. The model solves a simplified energy balance over the gasification process where the only reactions that are assumed to take place are the endothermic Equation (17) and the exothermic (18); these two are balanced so the heat released matches the heat required resulting in Equation (19) [22]. The heat of pyrolysis for the volatiles in the fuel is assumed to be 0.25MJ/kg and the latent heat of vaporization for water in the fuel 2.26MJ/kg, the fuel is assumed to be heated from 25°C to 850°C and the steam and oxygen mixture from 400°C to 850°C. The heat required for pyrolysis, vaporization and heating is assumed to be supplied by Equation (17). Since the possibility to introduce the steam needed for the water shift reactor, a process step in IGCC, directly into the fluidized bed wanted to be explored the required steam amount has to be known. This amount is based on Equation (20), where the amount of CO is based on the products of Equations (17) and (18). This extra steam is also assumed to be heated from 400°C to 850°C.

$$C + H_2O \rightarrow CO + H_2 \tag{17}$$
$$C + 0.5O_2 \rightarrow CO \tag{18}$$
$$2.2C + H_2O + 0.6O_2 \rightarrow 2.2CO + H_2 \tag{19}$$
$$CO + H_2O \rightarrow CO_2 + H_2 \tag{20}$$