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Review Article

Materials for Chemical-Looping with Oxygen Uncoupling

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Chemical-looping with oxygen uncoupling (CLOU) is a novel combustion technology with inherent separation of carbon dioxide. The process is a three-step process which utilizes a circulating oxygen carrier to transfer oxygen from the combustion air to the fuel. The process utilizes two interconnected fluidized bed reactors, an air reactor and a fuel reactor. In the fuel reactor, the metal oxide decomposes with the release of gas phase oxygen (step 1), which reacts directly with the fuel through normal combustion (step 2). The reduced oxygen carrier is then transported to the air reactor where it reacts with the oxygen in the air (step 3). The outlet from the fuel reactor consists of only CO_2 and H_2O, and pure carbon dioxide can be obtained by simple condensation of the steam. This paper gives an overview of the research conducted around the CLOU process, including (i) a thermodynamic evaluation, (ii) a complete review of tested oxygen carriers, (iii) review of kinetic data of reduction and oxidation, and (iv) evaluation of design criteria. From the tests of various fuels in continuous chemical-looping units utilizing CLOU materials, it can be established that almost full conversion of the fuel can be obtained for gaseous, liquid, and solid fuels.

1. Introduction

In the last decade, chemical-looping combustion (CLC) has emerged as a viable and efficient alternative for combustion with carbon capture. The interest in CLC is mainly due to the intrinsic separation of CO_2 from the rest of the flue gases during combustion, that is, nitrogen and unused oxygen, which means that no energy or equipment is needed for gas separation, which is in contrast to competing CCS technologies, that is, oxyfuel, postcombustion, and precombustion. An added advantage of CLC is the possibility to obtain 100% carbon capture, which is difficult to achieve in, for instance, post- or precombustion. Chemical-looping with oxygen uncoupling (CLOU) is very similar to CLC and has the same advantages with respect to efficiencies and degree of carbon capture, but the mechanism of fuel conversion is different, and this could result in significant advantages with respect to fuel conversion rates, which can have positive implications with respect to system performance. Below follows a description of both the CLC and CLOU technologies. This is followed by a simple thermodynamic analysis for some relevant metal oxides in Section 2. A detailed overview of the experimental research conducted on different oxygen carrier materials for CLOU is then carried out in Section 3. An overview of kinetic data for reduction and oxidation of CuO is given in Section 4, and Section 5 contains information with respect to the important design parameters, that is, solids inventory and recirculation rates. Finally, the paper is concluded with an outlook for the technology, including the main advantages and challenges.

1.1. Chemical-Looping Combustion (CLC). Chemical-looping combustion (CLC) is a technology for burning a fuel without mixing the combustion air and fuel [1–4]. This is done by using an oxygen carrier to transfer the oxygen from the air to the fuel, as is depicted in Figure 1. In this system, the fuel is introduced to the so-called fuel reactor, where an oxygen carrier reacts with the fuel according to the overall reaction,

$$(2n+m)\,Me_xO_y + C_nH_{2m} \longrightarrow (2n+m)\,Me_xO_{y-1} + nCO_2 + mH_2O \tag{1}$$

Here Me_xO_y and Me_xO_{y-1} are the fully oxidized and reduced forms of the oxygen carrier and C_nH_{2m} is the fuel and could be in gaseous, liquid, or solid form. The reduced oxygen

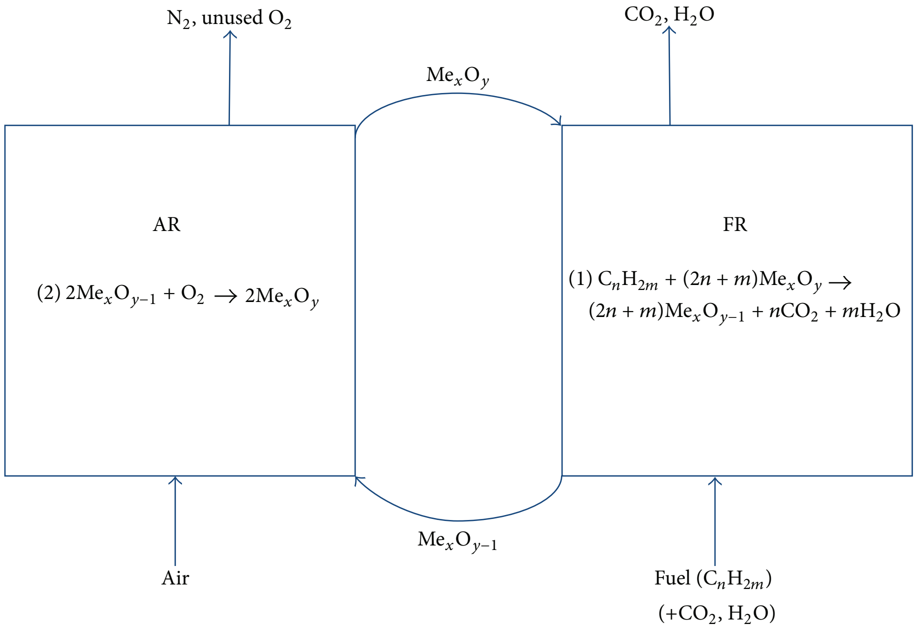


Figure 1: Schematic of the chemical-looping combustion (CLC) process. AR = Air reactor and FR = Fuel reactor.

carrier is transported to the air reactor, where it is reoxidized with the combustion air according to

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

The system of reactors in Figure 1 could be designed in a variety of ways, with the most common configuration being that of coupled fluidized beds where the oxygen carrier is the bed material. In 2001, Lyngfelt et al. [2] proposed a system which resembles that of a conventional circulating fluidized bed boiler (CFB), where the air reactor is a fast fluidized bed reactor and the fuel reactor is a bubbling fluidized bed reactor, and a schematic of such a boiler can be seen in Figure 2. In case of complete conversion of the fuel, the exhaust stream from the fuel reactor consists of only CO_2 and H_2O, from which pure CO_2 could be obtained after condensation of water. The reduced form of the oxygen carrier, Me_xO_{y-1}, is then transferred to the air reactor where it is reoxidized by air making it ready for the next cycle. The oxidation reaction is always exothermic while the reduction reaction can be exothermic or endothermic depending on the nature of the carrier and the fuel [5]. However, the sum of the enthalpy from reaction (1) and (2) is the same as for conventional combustion. Thus, the CLC process does not entail any direct cost or energy penalty for CO_2 separation. The basic idea of chemical-looping was proposed already in the 50s by Lewis et al. [6], but it was more or less forgotten until the 1990s when the group of Ishida et al. at the Tokyo Institute of Technology revived the process and conducted both process investigations and experimental studies of different oxygen carrier materials, for example, [1, 7–11]. At the start of the new millennium several groups initiated research on CLC with the aim of developing a combustion process with inherent CO_2 capture. The main research groups driving the developments at this time were Chalmers University of Technology in Sweden, [2, 12–14] ICB-CSIC, [15–18], Technical University of Vienna, [19–21], and Korea Institute of Energy Research, [22–25] although several other groups were also active at this time [26, 27]. Since then, the research around chemical-looping technologies has been steadily increasing, as can be gauged from the increase in the number of scientific articles published around the technology in the last decade.

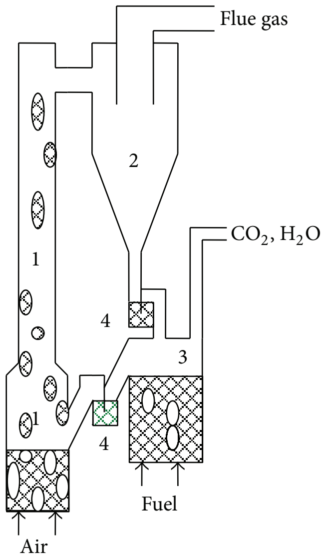


Figure 2: Chemical-looping combustion system designed with interconnected fluidized bed reactors similar to a circulating fluidized bed boiler (CFB). The oxygen carrier particles are transported from the air reactor (1), via the main cyclone (2) and particle lock (4) to the fuel reactor (3). The oxygen carrier particles are then returned to the air reactor via an overflow and additional particle lock.

The cornerstone of the CLC technology is finding oxygen carriers particles which are sufficiently reactive with fuel while at the same time having high mechanical stability over many redox cycles. The technology has been successfully demonstrated in a number of continuous units utilizing Fe- [28, 29], Mn- [30, 31], Cu- [32], and Ni-based oxygen carriers [33–37]. There are a number of recent reviews available on the status of CLC, whereof the more recent ones by Fan [38], Lyngfelt [39], and Adanez et al. [40]. There are also some reviews which are a few years old, for example, Lyngfelt et al. [41], Hossain and de Lasa [42], and Fang et al. [43]. These papers give a broad view of the different materials which have been investigated for CLC and also overviews of the operational experience. Most of the research around CLC has focused on gaseous fuels, such as natural gas and syngas consisting mainly of CO and H_2. This is not surprising, since this entails the least complex system and may also be the basis for the first full scale demonstration. When utilizing a gaseous fuel, such as CH_4, the overall reaction in the fuel reactor can be described by reaction (1). However, there could be many side or intermediate reactions in the fuel reactor, for instance, carbon deposition, water-shift reaction, and partial oxidation reactions, and it is likely that CO and H_2 are intermediate components, and small amounts may also be found in the outlet from the fuel reactor, for example, [28, 30, 37, 39, 44, 45]. It is important that oxygen carriers and conditions in the fuel reactor are employed which promote the full oxidation to CO_2 and H_2O. This means, for example, (i) use of an oxygen carrier with thermodynamic properties enabling conversion of gas to carbon dioxide and steam to a high extent, (ii) sufficient reaction rates with fuel, (iii) an oxygen carrier which has a sufficient lifetime and does not break down into smaller fragments at a high rate, and (iv) use of a cheap material.

There are only a limited number of studies focusing on utilizing liquid fuels, such as oil, with chemical-looping technologies [31, 46–49]. Of these, only two investigations have been performed where the fuel is directly injected into a circulating CLC system [31, 49]. Here kerosene was utilized as fuel and was evaporated prior to injection into the fuel reactor. It is likely that the evaporated fuel is reformed or decomposed to CO and H_2 in the fuel reactor before being fully oxidized to CO_2 and H_2O, similar to the processes for gaseous fuel. Looking forward, it is likely that heavier oil fractions would be of greater interest in CLC, and it may be more efficient to inject the fuel directly to the fuel reactor where evaporation and reactions with the oxygen carrier would occur in parallel.

In the case of solid fuels such as coal or biomass, the reaction pattern is more complex compared to when using gaseous or even liquid fuels [50]. One way to process solid fuel via CLC is to first perform an external gasification of the fuel to syngas and then process the syngas using gaseous CLC [51, 52]. As this would entail an external gasification unit and also an ASU for oxygen production for the partial gasification, it is questionable if it is an economically viable alternative. Instead, the fuel can be directly introduced into the fuel reactor together with the metal oxide particles [3, 53–55]. The fuel would here devolatilize to a gaseous fraction, that is, volatiles, and a solid char part, as is depicted in Figure 3. In parallel, the volatile part, composed mainly of CO, H_2, and CH_4, reacts directly with the oxygen carrier particles according to reaction (1). The char component is gasified in the presence of steam and carbon dioxide, producing CO and H_2 according to reactions (3) and (4)

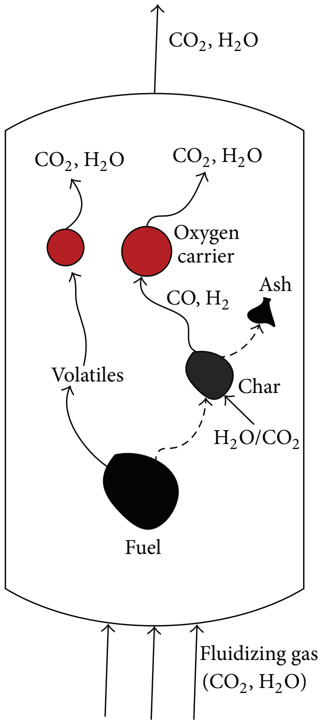


FIGURE 3: Reaction scheme in the fuel reactor for CLC with solid fuels.

$$\text{Char (mainly C)} + H_2O \longrightarrow CO + H_2 \quad (3)$$

$$\text{Char (mainly C)} + CO_2 \longrightarrow 2CO \quad (4)$$

The CO and H_2 from these reactions will then need to react with the oxygen carrier to fully oxidized products, as in reaction (1). Evidently, reactions (3) and (4) do not directly involve the oxygen carrier particles. Still, the rate of reactions (3) and (4) determines how well the solid fuel is converted to gas in the fuel reactor and governs the residence time of solids needed in the fuel reactor for full char conversion [54]. Insufficient residence time would lead to char being transferred to the air reactor where it would be burnt to carbon dioxide, thus decreasing the overall degree of CO_2 capture. The functionality of the oxygen carrier is associated with how well the particles are at converting the syngas generated to CO_2 and H_2O. In a well-mixed fuel reactor, the gasification reactions will take place in the entire reactor, meaning that there will be combustible components produced which have only limited contact with oxygen carrier particles, and thus it is expected that there will be CO and H_2 released from the fuel reactor even in a well-designed reactor [56]. It is also important that the volatiles have good contact with the oxygen carrier particles, which probably

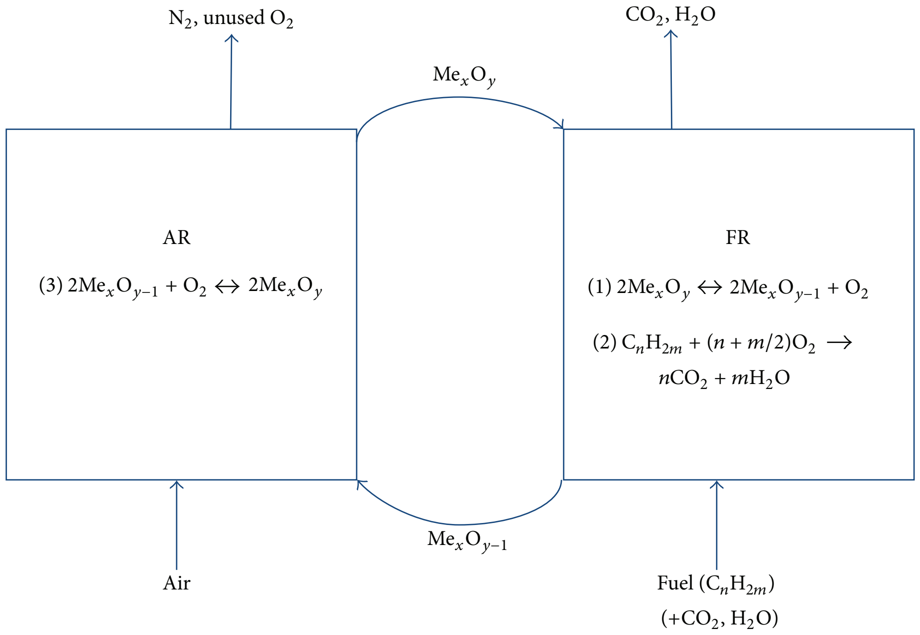


Figure 4: Principal layout of chemical-looping with oxygen uncoupling (CLOU). The oxygen carrier is denoted by Me_xO_y and Me_xO_{y-1}, where Me_xO_y is a metal oxide and Me_xO_{y-1} is a metal or a metal oxide with lower oxygen content compared to Me_xO_y. The fuel is here carbon (C). A fluidization gas, for example, recirculated CO_2 or steam, is most likely needed for the case of solid fuel.

means that the fuel needs to be introduced at the bottom of the fluidized fuel reactor. There are now many scientific articles related to the application of CLC for solid fuels, with investigations both in laboratory reactors, for example, [54, 57–59], and in continuous reactors, for example, [53, 60–64]. For a complete overview of the operational experience of CLC with solid fuels, the reader is referred to the reviews by Adanez et al. [40] and Lyngfelt [50]. Although several studies of CLC with solid fuels report on successful operation in continuous units, with high degrees of carbon capture, [64] the gas conversion levels are typically less than 95% [39]. The incomplete combustion may be due to imperfect contact between oxygen carrier particles and reacting gas, in addition to the presence of reacting char particles at the top of the well-mixed fuel reactor. However, Tong et al. reported CO_2 purity levels of 99.7% utilizing solid fuels with a moving-bed arrangement of the fuel reactor and employing rather large size particles [63]. There are several possibilities to solve the problem of low gas conversion, including installation of a postcombustion chamber downstream from the fuel reactor, using a multistaged fuel reactor or separation and recycling of the gases to the fuel reactor. All of these solutions entail installation of additional components and will result in added costs for the overall process. Another option is to utilize oxygen carrier materials which release O_2 in the gas phase, that is, chemical-looping with oxygen uncoupling (CLOU), which is the topic of this paper. By using CLOU, the main mechanism for fuel conversion is changed completely, as the gasification reactions (3) and (4) are eliminated and replaced by a much faster combustion process, which has positive implications for both the char and gas conversions.

1.2. Chemical-Looping with Oxygen Uncoupling (CLOU).

Chemical-looping with oxygen uncoupling (CLOU) is very similar to normal CLC, with the major difference that the process utilizes oxygen carriers which can release gas-phase oxygen in the fuel reactor; see Figure 4 [65]. In this way, the fuel reacts directly with gaseous oxygen released from the oxygen carrier, via normal combustion. The oxygen carrier releases oxygen through the decomposition of the oxidized form of the metal oxide, Me_xO_y, through (Step 1)

$$2Me_xO_y \longleftrightarrow 2Me_xO_{y-1} + O_2 \tag{5}$$

This is followed by the normal combustion of the fuel via (Step 2)

$$C_nH_{2m} + \left(n + \frac{m}{2}\right)O_2 \longrightarrow nCO_2 + mH_2O \tag{6}$$

The reduced oxygen carrier is transferred to the air reactor for reoxidation (Step 3). The net heat of reaction for the CLOU processes is the same as CLC; only the mechanism by which oxygen is accessed by the fuel differs. In CLOU, there is no direct reaction between fuel gas and the oxygen carrier, as is the case with normal CLC; see reaction (1). When using solid fuels like coal, the CLOU process avoids the slow gasification step of the char, reactions (3) and (4), and instead the reaction in the fuel reactor is composed of an oxygen uncoupling reaction (5) and normal combustion, reaction (6).

The CLOU process was proposed by Lyngfelt and Mattisson in 2005 [66], with some publications on the subject a few years later [65, 67, 68]. Here, several monometallic oxide systems were proposed as feasible oxygen carrier materials, that is, CuO, Mn_2O_3 and Co_3O_4 [65]. A thermal analysis was performed showing that CuO and Mn_2O_3 were most promising, as they showed a combination of reasonably high partial pressure of oxygen at relevant temperatures in addition to an exothermic reaction in the fuel reactor, which could result in a temperature increase in the fuel reactor. An increase in temperature could be of significant advantage, as it would promote the oxygen release rate. Experiments were also performed in a batch fluidized bed reactor with coal and petroleum coke utilizing Cu-based oxygen carrier particles. The overall CLOU reaction rate was shown to be governed by the oxygen release reaction (5) and the combustion reaction (6), and two limiting cases could be observed:

(i) the rate of oxygen release, or uncoupling, from the metal oxide is faster than the oxygen consumption by combustion reaction, resulting in oxygen being released from the exit of the reactor at a partial pressure approaching equilibrium, and

(ii) the rate of oxygen consumption by combustion exceeds that of the release rate through metal oxide decomposition, resulting in an outlet oxygen concentration approaching zero. Here, the char particles in the well-mixed bed of metal oxide particles reacted instantly with the released gas-phase oxygen, thus removing the equilibrium restriction for oxygen release, and hence increasing the driving force for reaction (5). The oxygen tied up with the combustion products CO_2 and H_2O was considerably higher than the amount which could be released if the reaction was limited by the equilibrium partial pressure of O_2 from reaction (5). An illustrative example of the enhanced rate of reaction possible with CLOU compared to CLC was provided in [65]. Here, it was shown that a batch of petroleum coke was converted approximately 50 times faster in a bed of CuO/ZrO_2 particles via the CLOU mechanism, compared to the rate of fuel conversion obtained in a bed of $Fe_2O_3/MgAl_2O_4$ particles fluidized by steam. The difference in conversion rates was attributed to the different mechanisms of fuel conversion between CLC and CLOU as described previously.

Oxygen carriers for CLOU need to fulfil many of the same criteria as normal CLC oxygen carriers; for example, the particles need to be mechanical stable, have limited tendencies for agglomeration, and be cheap. In addition, CLOU particles have special thermodynamic and kinetic requirements in comparison to oxygen carriers used in normal CLC; more specifically, consider the following.

1. The metal oxide should release gaseous oxygen and have a sufficient equilibrium partial pressure of oxygen at temperatures utilized during combustion in order to promote the rate of oxygen generation for complete burnout of the fuel.
2. The oxide system needs to have an equilibrium partial pressure low enough for oxidation at a reasonable oxygen concentration in the air reactor. This concentration is dependent upon the air ratio employed, but may need to be below approximately 5%O_2. A higher partial pressure out from the air reactor would mean lower efficiencies due to heat losses with the flue gases.
3. The reactions in the fuel reactor should preferably be exothermic, as this would result in a temperature increase, which will promote the release rate of gas-phase oxygen.

For the CLOU process, it is important to consider the important interplay between oxygen partial pressure of the metal oxide system, the heats of reaction, and the temperature in the reactors.

In the next section, a thermodynamic analysis for some monometallic oxygen carriers and one promising mixed oxide particle is performed. Further, a thermal analysis is carried out for CuO in order to establish the magnitude of the possible temperature rise in the fuel reactor.

2. Thermodynamic Aspects of CLOU

2.1. Equilibrium Partial Pressure of O_2. In a thermodynamic analysis of oxygen carriers for CLC, Jerndal et al. [5] showed that the oxide pairs CuO-Cu_2O, Mn_2O_3-Mn_3O_4, and Co_3O_4-CoO were not possible to use as oxygen carriers for CLC at higher temperatures due to decomposition of the most oxidized phase. Later, Mattisson et al. [65] identified these same systems as possible candidates for CLOU. Of these, CuO has received the most attention and seems to be the most promising with respect to the rate of oxygen release, for example, [69–72]. Rydén et al. recently reviewed the thermodynamics of a number of combined oxide systems [73], some of which now have experimentally proven CLOU properties [74–76]. The monometallic oxides of Cu, Mn, and Co release oxygen in the fuel reactor through reactions (7)–(9) below. Reaction (10) shows the decomposition reaction for a combined oxide system of $(Mn_yFe_{1-y})O_x$ which has shown promise as a CLOU material both thermodynamically and experimentally [74].

$$4CuO \longleftrightarrow 2Cu_2O + O_2\,(g) \qquad \Delta H_{850} = 263.2\,\text{kJ/mol } O_2 \tag{7}$$

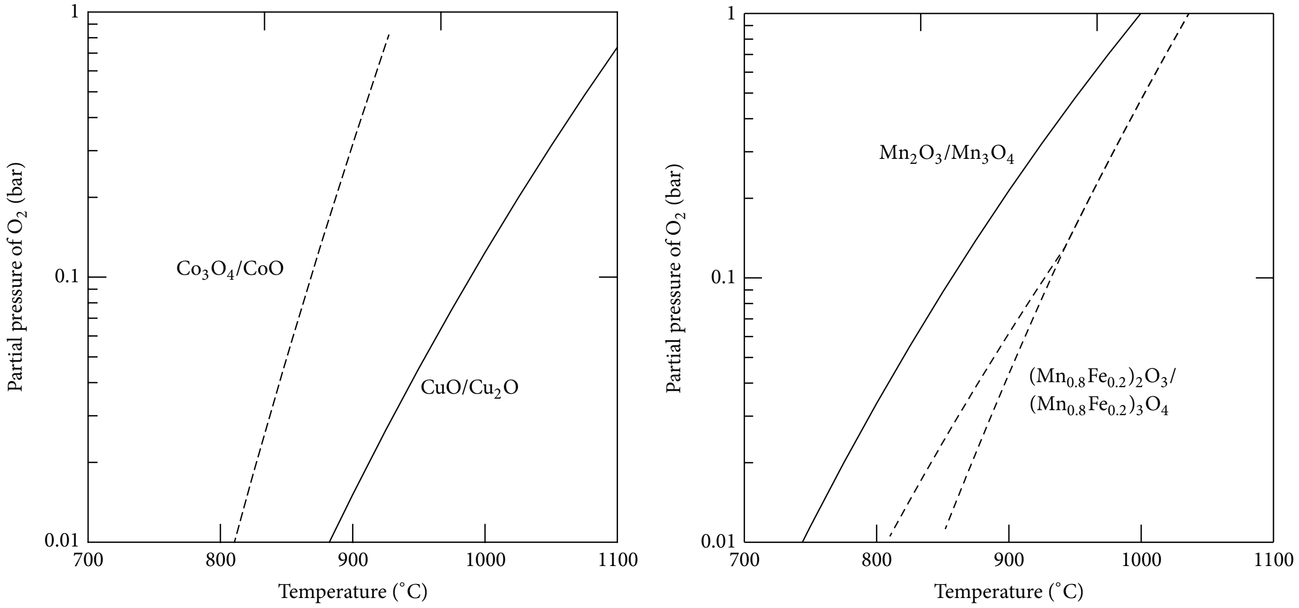
$$6Mn_2O_3 \longleftrightarrow 4Mn_3O_4 + O_2(g) \qquad \Delta H_{850} = 193.9\,\text{kJ/mol } O_2 \tag{8}$$

$$2Co_3O_4 \longleftrightarrow 6CoO + O_2\,(g) \qquad \Delta H_{850} = 408.2\,\text{kJ/mol } O_2 \tag{9}$$

$$\begin{gathered}6(Mn_{0.8}Fe_{0.2})_2O_3 \longleftrightarrow 4(Mn_{0.8}Fe_{0.2})_3O_4 + O_2\,(g)\\ \Delta H_{850} = 254\,\text{kJ/mol } O_2\end{gathered} \tag{10}$$

The equilibrium constant for the above reactions is given by

$$K_c = \frac{p_{O_2} a^n_{Me_xO_{y-1}}}{a^m_{Me_xO_y}}. \tag{11}$$



(a)

(b)

Figure 5: The partial pressure of gas-phase O_2 over the metal oxide systems (a) CuO/Cu_2O and Co_3O_4/CoO and (b) Mn_2O_3/Mn_3O_4 and $(Mn_{0.8}Fe_{0.2})_2O_3/(Mn_{0.8}Fe_{0.2})_3O_4$ as a function of temperature.

Assuming that the activity of 1 for both forms of the metal oxide, the partial pressure of O_2 can simply be equated with the equilibrium constant, that is,

$$p_{O_2} = K_c. \tag{12}$$

Figures 5(a) and 5(b) show the equilibrium partial pressure of O_2 as a function of temperature for the above reactions. From these two figures, it can be seen that CuO releases oxygen in air ($p_{O_2} = 0.21$ bar) at temperatures above 1028°C, Mn_2O_3 at temperatures above 899°C, Co_3O_4 above 889°C, and $(Mn_{0.8}Fe_{0.2})_2O_3$ above 960°C. For the combined oxide system of $(Mn_{0.8}Fe_{0.2})_2O_3$, there are two parallel curves which converge at higher temperatures, which are due to the presence of a two-phase region where both the oxidized and reduced oxides exist [74]. In the air reactor, however, the oxygen carrier needs to react with air and reduce the oxygen concentration in the outlet to a reasonable level, given by the excess air ratio [2],

$$\lambda = \frac{0.21\left(1 - x_{O_2,\mathrm{ex}}\right)}{0.21 - x_{O_2,\mathrm{ex}}}, \tag{13}$$

where $x_{O_2,\mathrm{ex}}$ is the outlet volume fraction of oxygen from the air reactor. Although the air ratio could be adjustable, in order to achieve an efficient process, it should probably be in the range 1.1–1.3, which corresponds to an outlet oxygen volume fraction of 2–6% in the outlet stream from the air reactor. Of course, a higher air ratio is possible, but will result in considerable heat losses and subsequently a less efficient process. For basis of the following discussion, it will be assumed that the oxygen concentration in the outlet should not exceed 5%. Thus, considering the equilibrium partial pressures in Figure 5, a CLOU system utilizing oxygen carriers of CuO, Mn_2O_3, Co_3O_4, and $(Mn_{0.8}Fe_{0.2})_2O_3$ the maximum temperature in the air reactor is 955°C, 820°C, 850°C, and 890°C, respectively. A higher temperature would likely mean that the outlet from the air reactor would contain more than 5%O_2, which may be uneconomical in a power plant. When the particles are transferred to the fuel reactor, it is of course an advantage if the temperature is as high as possible, as this would promote the rate of oxygen release. This depends upon the thermal nature of the overall reaction in the fuel reactor, and this will be explored below.

2.2. Thermal Considerations.

When the oxygen carrier material is transferred to the fuel reactor, the oxygen carrier should release oxygen which will react with the fuel. Considering that the total heat evolved from a CLOU system will be that of normal combustion, the sum of the heats of reaction in the fuel and air reactor will be that of normal combustion. In Table 1, the reaction enthalpies of the oxidation reactions (7)–(10) are given, in addition to the combustion enthalpies of C, CH_4, and a common coal per mol O_2. The ratio between the reaction and combustion enthalpy shows whether the reaction in the fuel reactor is endothermic or exothermic; a ratio above 1 would mean that the reaction is endothermic while a ratio below 1 would mean an exothermic reaction. From Table 1, the ratio is below 1 for CuO, Mn_2O_3, and $(Mn_{0.8}Fe_{0.2})_2O_3$, meaning that the overall reaction in the fuel reactor must be exothermic, which will result in a temperature increase in this reactor. For Co_3O_4, however, the ratio is slightly above 1 for C and CH_4, meaning that the reactions in the fuel reactor are slightly endothermic,

Table 1: Reaction enthalpies for combustion and oxidation reactions.

	ΔH_{850} (kJ/mol O_2)	$\Delta H/\Delta H_{\text{comb } CH_4}$	$\Delta H/\Delta H_{\text{comb C}}$	$\Delta H/\Delta H_{\text{comb coal}}$
$O_2 + 1/2CH_4 \rightarrow 1/2CO_2 + H_2O$	−401.0	1.00		
$O_2 + C \rightarrow CO_2$	−394.8		1.00	
$O_2 + 1.5C_{0.57}H_{0.40}O_{0.03}{}^{*} \rightarrow 0.87CO_2 + 0.3H_2O$	−410.4			1.00
$O_2 + 2Cu_2O \rightarrow 4CuO$	−263.2	0.66	0.67	0.64
$O_2 + 4Mn_3O_4 \rightarrow 6Mn_2O_3$	−193.9	0.48	0.49	0.47
$O_2 + 6CoO \rightarrow 2Co_3O_4$	−408.2	1.02	1.03	0.99
$4(Mn_{0.8}Fe_{0.2})_3O_4 + O_2\ (g) \rightarrow 6(Mn_{0.8}Fe_{0.2})_2O_3 + O_2\ (g)$	-254^1	0.63	0.64	0.62

[1] Data taken from Rydén et al. [73]. *Common coal. Data taken from [131].

Table 2: Mass and heat balance of the fuel reactor.

	Incoming (mol)	Products (mol)	c_p (J/mol, °C)	$C_{p,\text{prod}}$ (J/°C)
CuO	20	16	56.7	907.2
C	1		—	
Cu_2O		2	85.2	170.2
CO_2 (reaction)		1	56.7	56.7
	$\sum C_{p,\text{prod}}$			1134.3

and thus there will be a temperature decrease for Co_3O_4. Although the reaction is slightly exothermic for the analyzed coal and cobalt oxide, considering heat losses and that heat will be needed to pre-heat the fluidization gas, there will likely be a temperature drop also for coal. The fact that a temperature increase is possible for most oxide systems is significant and of considerable advantage for the following reasons: (i) the higher temperature will promote the oxygen release rate from the metal oxide particles and (ii) the recirculation rate of particles between the air and fuel reactor can be kept low, as the recirculating particles do not need to provide heat for an endothermic reaction, which is the case for CLC with solid fuels [54]. The temperature drop in the fuel reactor for the cobalt oxide in combination with its high cost and toxicity likely makes this oxygen carrier unsuitable for a CLOU system.

The magnitude of a possible temperature increase will be illustrated with a simple mass and heat balance using CuO as an oxygen carrier. Assuming that the fuel is pure C, the overall reaction in the fuel reactor is

$$4CuO + C \longrightarrow 2Cu_2O + CO_2(g) \quad \Delta H_{925} = -133.4 \text{ kJ/mol} \tag{14}$$

In the calculations, it is assumed that 1 mol C is burnt in the fuel reactor. Further assumptions are (i) the reactor is adiabatic, (ii) the particles from the air reactor are fully oxidized and at a temperature of 925°C, which is the temperature of the particles which enter the fuel reactor, (iii) 20% of the CuO is converted to Cu_2O in the fuel reactor, and (iv) the reactor is fluidized with 0.5 moL CO_2 which is at a temperature of 400°C. A summary of the mass balance can be seen in Table 2, where the total heat capacity of the products, $C_{p,\text{prod}}$, is also calculated to be 1134.3 J/°C. Taking into account that approximately 35 kJ is needed to heat the fluidization gas and the fuel to the reaction temperature, then the temperature increase can be estimated from

$$\Delta T \approx \frac{\Delta H}{C_{p,\text{prod}}} = \frac{98400\text{ J}}{1134.3\text{ J}/{}^{\circ}\text{C}} = 87\,{}^{\circ}\text{C}. \tag{15}$$

Thus, the actual temperature in the fuel reactor would approach 1012°C. From Figure 5(a), this corresponds to an O_2 partial pressure of 15%. The increase in temperature will promote the overall reaction rate in the fuel reactor, as the rate of oxygen decomposition is governed by the equilibrium partial pressure of O_2 and a reaction rate constant, see (18), both of which likely increase as a function of temperature. A more detailed mass balance of the CLOU system was carried out by Mattisson et al. [65] and Eyring et al. [77]. Sahir et al. performed a process simulation on both a CLC and CLOU systems utilizing Fe_2O_3 and CuO, respectively [78]. The main advantages with the CLOU system were identified to be the lower residence time of solids in the fuel reactor and the possibility to extract heat from the fuel reactor due to the exothermic reactions. In association with the CLOU concept, there have been several articles which have proposed using the reversible redox reaction (5) for production of gaseous oxygen [79, 80]. As fuel would not be added to the fuel reactor, the reaction in the fuel reactor would be endothermic with a resulting temperature drop, and hence the driving force for oxygen release would not be promoted, as is the case with CLOU. Further, as there is no fuel to remove the gaseous oxygen through combustion, the oxygen partial pressure during the decomposition may be limited to the equilibrium partial pressure at the temperature employed.

3. Overview of Experimental Investigations of CLOU Materials

The first experimental work on CLOU was published in 2008 and 2009 [65, 67, 68], where the CLOU concept was shown using a Cu-based oxygen carrier with gas and solid fuels. It should be mentioned that already in the original work on chemical-looping by Lewis et al. in 1951, coke was combusted with a Cu-based oxygen carrier, and it was suggested that part of the fuel was converted by uncoupled gas-phase oxygen [6]. In the last five years, there have been a large number of articles published with experimental investigations of different oxygen carrier materials, mostly based on Cu and Mn oxides. Table 3 contains a complete overview of the experimental investigations of CLOU materials. Adanez et al. [40] provided an overview of CLOU materials in 2011, and this table is basically an update of this overview. It should be noted that only articles which have the aim of utilizing the oxygen uncoupling behaviour of metal oxide particles are presented in Table 3. Further, several conference papers are not included, as the results are presented in follow-up journal articles. Most of the investigations have been carried out at Chalmers University of Technology in Sweden and at ICB-CSIC in Zaragoza, Spain, but there are currently several other groups working with the development of the CLOU process, including research groups at the University of Utah in the United States, Tsinghua University in China, and Swiss Federal Institue of Technology in Switzerland. Below follows an overview of the research presented in Table 3.

3.1. Copper Oxide. Copper oxide has received a great deal of attention as an efficient oxygen carrier both for CLC and CLOU applications, owing to its high reactivity, high oxygen transport capacity, and absence of thermodynamic limitation for complete combustion of hydrocarbon fuels. With respect to CLC, the CuO can be reduced all the way to Cu via

$$(2n+m)\,\mathrm{CuO} + \mathrm{C}_n\mathrm{H}_{2m} \longrightarrow (2n+m)\,\mathrm{Cu} + n\mathrm{CO}_2 + m\mathrm{H}_2\mathrm{O} \quad (16)$$

Most research around the use of CuO for CLC has focused on this direct reaction between fuel and oxygen carrier. Investigations have been carried out with different types of gaseous and solid fuels in batch fluidized bed reactors [58, 70, 81–88], fixed-bed reactors [89, 90], thermogravimetric reactors [13, 15–17, 91–93], and interconnected fluidized beds with continuous circulation of the oxygen carrier material [32, 94]. Despite the rather promising results found in the studies of Cu materials for CLC, the use of CuO as an oxygen carrier is not without limitations. For example, copper oxide suffers from tendency towards agglomeration upon full reduction, due to the formation of elemental copper which has a rather low melting temperature (1085°C) [81].

When utilizing copper materials for CLOU, metallic Cu should not be formed, but it is the redox pair CuO-Cu_2O which is active; see reaction (14). Most experimental studies around CLOU have been conducted with CuO as the active material [68–72, 77, 95–102]. Although there certainly could be an oxygen uncoupling effect also in some of the previously mentioned studies of CuO for CLC, the investigations in Table 3 were specifically aimed at utilizing the uncoupling effect possible when cycling between CuO and Cu_2O.

Mattisson et al. demonstrated the CLOU concept using oxygen carriers of CuO/Al_2O_3 and CuO/ZrO_2 with both gaseous and solid fuels in a batch fluidized bed reactor [65, 67, 68]. Figure 6 shows the concentration profiles for one such experiment where 0.1 g of petroleum coke reacted with 15 g of CuO/ZrO_2 particles which were fluidized with N_2. Initially, the particles are exposed to air (O*x*), but at 25 s the air is replaced with nitrogen, and the outlet oxygen concentration drops and approaches the equilibrium concentration. At approximately 70 s the petroleum coke is introduced to the fluidized bed and the fuel mixes with the oxygen carrier particles. The char reacts rapidly with the released O_2 to form CO_2. There are some small peaks of CH_4 and CO initially due to release of volatiles, which are not shown in the figure. The oxygen concentration drops during the reduction but does not go down to zero, and at the same time the CO_2 volume fraction is high, approaching 51%. This means that the thermodynamic barrier for the decomposition of CuO to Cu_2O is removed and that the release of O_2 from the particles is faster than the consumption of O_2 through combustion. Complete burnout of the petroleum takes about 30 s, after which the oxygen concentration again approaches equilibrium. The rate of char conversion observed in this experiment is a 45-fold increase to that observed utilizing a Fe-based oxygen carrier without CLOU properties [54]. Leion et al. [67] performed CLOU experiments with the same oxygen carrier in a batch fluidized bed using a lignite coal in the temperature range of 850–985°C and found similarly enhanced reaction rates. The oxidation reaction occurred close to the equilibrium O_2 concentration for these particles. In a follow-up investigation by Leion et al. [103], six different solid fuels were investigated together with petroleum coke,

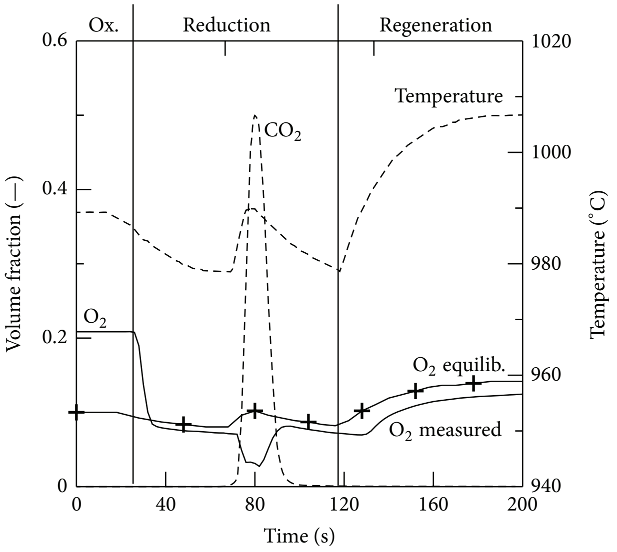


FIGURE 6: Volume fraction of CO_2 and O_2 as well as measured temperature for a CLOU experiment in a batch fluidized bed reactor, where 0.1 g petroleum coke reacted with 15 g CuO/ZrO_2 oxygen carrier. The O_2 concentration during regeneration of the oxygen carrier is 21%. The set-point temperature is 985°C and the fluidizing gas is pure nitrogen. Also included is the equilibrium concentration of O_2, as determined from the temperature measurement in the bed (+). Taken from [68].

Table 3: Overview of oxygen carriers investigated for chemical-looping with oxygen uncoupling (CLOU)

Authors	Reference	Oxygen carrier (OC) (Me_xO_y/support)	Prep. method (OC)	Fuel	T_{CLOU} (°C)[1]	Apparatus	Notes[2]
Leion et al., 2008	[67]	CuO/ZrO_2	FG	Lignite	850–985	FzB	b, d
Mattisson et al., 2009	[65]	CuO/Al_2O_3, CuO/ZrO_2	FG	CH_4, petcoke	950, 985	FzB	
Mattisson et al., 2009	[68]	CuO/ZrO_2	FG	Petcoke	885–985	FzB	d
Leion et al., 2009	[103]	CuO/ZrO_2	FG	petcoke, coal, and wood char	950	FzB	
Shulman et al., 2009	[76]	Mn_3O_4/Fe_2O_3, Mn_3O_4/NiO, Mn_3O_4/SiO_2	FG	CH_4	810–900	FzB	b
Leion et al., 2009	[123]	$CaMn_xTi_{1-x}O_3$	SP, FG	CH_4, petcoke	630–1000	TGA, FzB	b
Arjmand et al., 2011	[70]	CuO/Al_2O_3, $CuO/MgAl_2O_4$	FG	CH_4	900–925	FzB	b, d
Azimi et al., 2011	[111]	Mn_3O_4/Fe_2O_3	SD	CH_4 syngas, petcoke, and and coal	900–1000	FzB	
Eyring et al., 2011	[77]	CuO	—	—	750–950	TGA	a, b, d, e
Rydén et al., 2011	[114]	Manganese ore, Mn_3O_4/Fe_2O_3	SD	CH_4	780–1000	CFzB	b
Rydén et al., 2011	[75]	$CaMn_{0.875}Ti_{0.125}O_3$	FG	NG	620–950	CFzB	b
Shulman et al., 2011	[108]	Mn_3O_4/MgO, $Mn_3O_4/MgO/Ca(OH)_2$, $Mn_3O_4/MgO/TiO_2$	FG	CH_4	810–950	FzB	b
Abad et al., 2012	[69]	$CuO/MgAl_2O_4$	SD	Bituminous coal	900–960	CFzB	
Adanez-Rubio et al., 2012	[97]	$CuO/MgAl_2O_4$	SD	—	900–1000	TGA, FzB, CFzB	b, d
Adanez-Rubio et al., 2012	[95]	$CuO/MgAl_2O_4$	SD	Bituminous coal	900–980	FzB	
Adanez-Rubio et al., 2012	[132]	$CuO/MgAl_2O_4$	SD	Lignite	900–935	CFzB	c
Arjmand et al., 2012	[71]	$CuO/MgAl_2O_4$	FG	Biomass char	850–900	FzB	a, d
Arjmand et al., 2012	[115]	Manganese ore	—	Petcoke	970	FzB	
Arjmand et al., 2012	[116]	Manganese ore	—	CH_4, syngas, petcoke, and biomass char	900–950	FzB	
Azimi et al., 2012	[113]	Mn_3O_4/Fe_2O_3	SD	Biomass char	850	FzB	
Gayán et al., 2012	[72]	CuO/Al_2O_3, $CuO/MgAl_2O_4$, CuO/Sepiolite, CuO/SiO_2, CuO/ZrO_2, CuO/TiO_2, CuO/MgO	I, MM	—	900–1000	TGA, FzB	b
Hedayati et al., 2012	[104]	CuO/CeO_2, $CuO/Ce_{0.9}Gd_{0.1}O_{1.9}$, Mn_2O_3/CeO_2	E	CH_4 syngas	900–950	FzB	b
Imtiaz et al., 2012	[99]	$CuO/MgAl_2O_4$, CuO/CeO_2, CuO/Al_2O_3,	CP	CH_4	900–950	FzB, TGA	b
Jing et al., 2012	[107]	Mn_3O_4/SiO_2, $Mn_3O_4/Fe_2O_3/SiO_2$	SD	CH_4 syngas	900–950	FzB	b
Källén et al.,	[124]	$CaMn_{0.9}Mg_{0.1}O_3$	SD	NG	750–950	CFzB	b
Moldenhauer et al., 2012	[31]	CuO/ZrO_2, $Mn_3O_4/Mg\text{-}ZrO_2$	SD	Kerosene	700–975	CFzB	b
Rydén et al., 2012	[133]	Ilmenite	—	—	950	CFzB, FzB	b

Table 3: Continued.

Authors	Reference	Oxygen carrier (OC) (Me_xO_y/support)	Prep. method (OC)	Fuel	T_{CLOU} (°C)[1]	Apparatus	Notes[2]
Wen et al., 2012	[101]	Cu-ore	—	—	800–1050	TGA, FzB	b, d
Whitty and Clayton, 2012	[102]	CuO/SiO_2, CuO/TiO_2, CuO/ZrO_2	FG, MM, I	—	750–1000	TGA, FxB, FzB	a, b, d
Adanez-Rubio et al., 2013	[96]	$CuO/MgAl_2O_4$	SD	Anthracite, bituminous, and lignite	900–950	CFzB	
Arjmand et al., 2013	[125]	$Ca_xLa_{1-x}Mn_{1-y}MyO_{3-\delta}$ (M = Fe, Ti, Mg, Cu)	E	CH4, syngas, and biomass char	900–1000	FzB	a, b
Arjmand et al., 2013	[134]	$CuO/MgO\text{-}ZrO_2$, $CuO/CeO_2\text{-}ZrO_2$, $CuO/CaO\text{-}ZrO_2$	FG	CH_4	900–925	FzB	b
Azad et al., 2013	[118]	CuO/Mn_2O_3	E	CH_4	800–850	FzB	b
Azimi et al., 2013	[112]	Mn_3O_4/Fe_2O_3	SD	CH_4 syngas	850–950	FzB	b
Azimi et al., 2013	[74]	$(Mn_{0.8}Fe_{0.2})_2O_3$	SD	CH_4, biomass char	850	FzB	b
Jing et al.	[105]	CuO/ZrO_2, $CuO/ZrO_2/La_2O_3$, $CuO/Y\text{-}ZrO_2$, $CuO/MgAl_2O_4$, $CuO/MgAl_2O_4/La_2O_3$, CuO/CeO_2, $CuO/CeO_2/La_2O_3$, CuO/Mn_2O_3, CuO/Fe_2O_3, $CuO/Fe_2O_3/Mn_2O_3$, $CuO/Fe_2O_3/MgO$, $CuO/Fe_2O_3/Al_2O_3$, Mn_3O_4/MgO, $CaMn_xX_{1-x}O_3$ $Ca_xMn_yX_zO_3$	SD	CH_4, syngas	900–950	FzB	b
Song et al., 2013	[100]	CuO/Al_2O_3	CP	CO	800–1000	FzB	b

[1] The temperature generally refers to the temperature used during the decomposition (uncoupling) reaction or the temperature in the fuel reactor. [2] Notes: (a) kinetic/reactivity investigation, (b) investigation of oxygen release in inert atmosphere, (c) investigated effect of sulphur, (d) oxidation reaction investigated, and (e) used commercial powder of CuO.

Abbreviations: SD: spray drying, FG: freeze granulation, MM: mechanical mixing, E: extrusion, CP: coprecipitation, I: impregnation, and SP: spray pyrolysis. NG: Natural gas.

FzB: Batch fluidized bed reactor, CFzB: continuous interconnected fluidized bed reactor, FxB: fixed-bed reactor, and TGA: thermogravimetric analyzer.

coal, and wood char with the same CuO/ZrO_2 material. Also, here considerably higher conversion rates were found for CLOU compared to rates with ilmenite as oxygen carrier. The difference in fuel conversion rates was more pronounced for the low volatile fuels, such as, petroleum coke.

In the most extensive screening study of Cu-based oxygen carriers for CLOU to date, Gayán et al. prepared 27 different materials of CuO with different support materials using impregnation and mechanical mixing. Of these, the oxygen release characteristics of 25 materials were tested using TGA and a batch fluidized bed reactor [72]. The most promising materials were composed of CuO with ZrO_2 and CuO on $MgAl_2O_4$. From this screening study, the same group of researchers prepared a material based on 60 wt% CuO with $MgAl_2O_4$ using spray drying, and this material has been investigated using a number of different experimental units and conditions. The oxygen carrier was tested with coal in a continuously operated CLOU unit, showing proof of the concept of CLOU using solid fuels [69, 98]. Here, complete combustion was found using an oxygen carrier inventory in the fuel reactor of 235 kg/MWth. As mentioned previously, most earlier studies of CLC with solid fuels have resulted in incomplete combustion, with combustible components released from the fuel reactor. The investigation by Abad et al. shows that complete gas conversion is possible using oxygen carrier particles with CLOU properties. Several other studies have found that CuO with $MgAl_2O_4$ is highly promising as a CLOU material [70, 71, 95–97]. Arjmand et al. compared the feasibility of using CuO with Al_2O_3 and $MgAl_2O_4$ as support and found that CuO combines readily with Al_2O_3 to form $CuAl_2O_4$ which does not have CLOU properties [70]. Adanez-Rubio et al. tested the combustion of four different types of coal in a continuously operated CLOU unit at temperatures of 900–950°C using a spray-dried oxygen carrier of CuO with $MgAl_2O_4$ [96]. Complete combustion was attained for all coals, with no unburnt in the off-gases.

Although the results with CuO with $MgAl_2O_4$ appear highly promising with respect to reactivity, Adanez-Rubio et al. also report that the particles increase in porosity as a function of time and hence lose mechanical strength [97].

Most investigations of CuO materials have utilized particles with $MgAl_2O_4$ or ZrO_2 as support, as seen from Table 3, but there are also studies of Cu materials for CLOU utilizing natural materials [101] as well as other support materials [99, 102, 104, 105]. For instance, Hedayati et al. used CuO with CeO_2 and $Ce_{0.9}Gd_{0.1}O_{1.9}$ prepared by extrusion [104]. The particles were investigated in a batch fluidized bed reactor with respect to oxygen release behaviour and reactivity with CH_4 and syngas. The oxygen carrier utilizing the Gd-doped support showed the best results, and complete conversion of both CH_4 and syngas could be achieved in the batch fluidized reactor which was used to test the material.

3.2. Combined Oxides. The monometallic systems of CuO/Cu_2O and Mn_2O_3/Mn_3O_4 clearly have interesting properties which make them suitable for CLOU applications. The disadvantage with utilizing Cu material is the relatively high cost of Cu in addition to the low melting temperature of copper. Further, manganese oxides suffer from the apparent slow kinetics of Mn_3O_4 to Mn_2O_3 at the low temperature needed in order to oxidize the material fully; see Figure 5(b) [104, 106]. Recently, a number of articles have been published utilizing combined oxides as oxygen carriers for CLOU, for example, [74, 107, 108]. The common denominator for all of these investigated materials is that they contain manganese in the structure. These combined oxides have thermodynamic and/or kinetic properties which differ from pure Mn_2O_3 and which enable the decomposition of the oxide with release of gaseous oxygen at conditions suitable for CLOU. An example of this is the $(Mn_{0.8}Fe_{0.2})_2O_3/(Mn_{0.8}Fe_{0.2})_3O_4$ system. A comparison of the p_{O_2}-T function of this material with Mn_2O_3 in Figure 5(b) shows that it should be possible to oxidize the combined oxide at a higher temperature in the air reactor than what is possible for the pure oxide, and this may also affect the rate of oxidation. A thermodynamic analysis of many of these systems has been performed by Rydén et al. [73].

3.2.1. Mn-Fe-O. In an experimental study by Shulman et al., it was discovered that Mn_3O_4 combined with Fe_2O_3 performed very well as a CLOU oxygen carrier [76, 109]. Mn_3O_4-Fe_2O_3 particles with a molar ratio of Mn/(Mn+Fe) of 0.6 and 0.8 were produced by freeze granulation. Both oxygen carriers released oxygen in the gas phase in the temperature interval of 810–900°C. Reactivity experiments with methane in a fluidized bed reactor found that CH_4 reacted almost completely to CO_2 at 850 and 900°C for the material with the highest fraction Mn. It was speculated that the active phase was a combined metal oxide of the form $Fe_xMn_{1-x}O_3$. Oxygen carriers composed of Mn-Fe had earlier been tested by Lambert et al. [110], but the CLOU effect was not observed in this investigation. Azimi et al. [74, 111–113] has conducted extensive investigations of this system using spray-dried oxygen carriers and using both solid and gaseous fuels. In one investigation [112], an extensive number of Fe/Mn particles were tested with Mn/(Mn + Fe) from 0.2 to 0.8 using methane and syngas. The oxygen uncoupling effect was dependent on the Mn/Fe ratio and the temperature of oxidation and reduction. Oxygen carrier particles with an Mn/(Mn + Fe) ratio of 0.2–0.4 release oxygen at 900°C, whereas materials with a higher Mn content showed no oxygen uncoupling. On the other hand, at the lower temperature of 850°C materials with an Mn/(Mn + Fe) greater than 0.5 released considerable amounts of oxygen. The behaviour of these materials agreed well with what is expected based on the calculated phase diagram of the Fe-Mn-O system. The reactivity with methane followed the uncoupling properties well.

Rydén et al. [114] investigated two oxygen carriers with high contents of Mn and Fe in a continuous circulating CLC reactor. The first material was produced by spray drying and contained only Mn_3O_4 and Fe_2O_3 with a molar ratio of Mn/Fe of 2. The second material was a natural manganese ore with a relatively high content of Fe_2O_3 (>6.5%). Both materials had a CLOU effect in the temperature interval of 850–1000°C and a gas yield to CO_2 at 950°C of 96% and 76% for the synthetic and natural ore, respectively. These values were judged to be excellent compared to other types of material. The main problem was that both materials deteriorated and turned to very fine powder after several hours of combustion. This lack of mechanical stability seems to be a general problem with this system, as swelling and increased porosity was noted also by Shulman et al. [76]. Also Arjmand et al. [115, 116] found a small CLOU effect for several manganese ores at 950–970°C. Fossdal et al. [117] investigated a number of ores and industrial wastes as oxygen carriers for CLC. Among the tested materials, the redox properties of two Fe-Mn slags were investigated. The materials were not deemed promising as the oxygen carrying capacity and regenerability was poor. However, it is likely that the phase transition investigated was between $(Mn_xFe_{1-x})_3O_4$ and $(Mn_xFe_{1-x})O$, which is not of interest for CLOU.

3.2.2. Mn-Si-O. Rydén et al. presented a phase diagram of the Mn-Si-O system and identified several pathways for oxygen release [73]. The experimental investigations of this combined oxide system are very limited with respect to CLOU. Shulman et al. [76] prepared particles of 80 wt% Mn_3O_4 with SiO_2 by freeze granulation. The particles released oxygen in the gas phase in the temperature interval of 810–900°C. Interestingly, from XRD analysis of the samples calcined at 950°C and 1100°C, there did not seem to be any interaction between Mn_3O_4 and SiO_2. Jing et al. investigated spray-dried particles of Mn_3O_4/SiO_2 with varying content of Mn using a batch fluidized bed reactor [107]. Particles which contained more than 90% Mn_3O_4 showed no uncoupling at 900°C, whereas the samples containing 50 and 70 wt% Mn_3O_4 released oxygen in the inert period; that is, when the particles were fluidized with nitrogen. The highest degree of uncoupling was seen for a sample which also contained Fe_2O_3. The average gas conversion of methane to carbon dioxide varied between 70 and 98% at 950°C. Although no phase analysis was presented, the results were interpreted using the phase diagram presented by Rydén et al. [73].

3.2.3. Other Combined Oxide Systems. In addition to the combined manganese oxide systems of Mn-Fe-O and Mn-Si-O discussed above, a few studies have explored other similar mixed oxide systems. Azad et al. investigated the CLOU properties of oxygen carriers composed of Mn_2O_3 and CuO [118]. The authors found that there was a cooperative synergy between the Cu and Mn oxides, with formation of $Cu_xMn_{3-x}O_4$ during oxidation, which was reduced to $CuMnO_2$ and Mn_3O_4 with concomitant release of O_2 in the gas phase. The reactivity with CH_4 was investigated at 800 and 850°C in a batch fluidized bed reactor, and a high gas yield to CO_2 and H_2O was obtained at the higher temperature. In addition to the oxygen carriers of Mn-Fe and Mn-Si, Shulman et al. also tested materials based on Mn-Ni and Mn-Mg, and both systems showed interesting CLOU properties [76, 108].

3.2.4. Perovskites. Perovskites are a series of materials with the general formula ABO_3, where A is a large cation and B is a smaller cation. Perovskite materials exhibit interesting redox properties and have been investigated for both chemical-looping combustion (CLC) and chemical-looping with oxygen uncoupling (CLOU) [75, 119–122]. Oxygen carrier particles can exhibit oxygen nonstoichiometry and can release substantial amounts of oxygen via

$$ABO_{(3-\delta)_{\mathrm{AR}}} \longleftrightarrow ABO_{(3-\delta)_{\mathrm{FR}}} + \frac{1}{2}\left(\delta_{\mathrm{FR}} - \delta_{\mathrm{AR}}\right) O_2 \qquad (17)$$

The oxygen released in the gas phase, given by $(\delta_{\mathrm{FR}} - \delta_{\mathrm{AR}})$, can be used during CLOU process to burn gas, liquid, or solid fuel. The term "δ" gauges the degree of oxygen nonstoichiometry and "AR" and "FR" refer to the air and the fuel reactor, respectively. The oxygen nonstoichiometry of a perovskite material can be altered by changing parameters such as the ambient temperature, pressure, or the O_2 fugacity. For example, in the oxidizing environment of the air reactor, δ_{AR} is determined by the partial pressure of oxygen at the outlet of the reactor, which is typically around 5%. In the fuel reactor, the environment is reducing which translates to a very low O_2 activity; hence at equilibrium δ_{FR} is larger than δ_{AR} meaning that there will be a release of gaseous oxygen.

With respect to CLOU, the focus has been on the calcium manganate system, $CaMnO_{3-\delta}$, which has shown to exhibit a combination of high mechanical stability, good fluidization properties, and well good reactivity with gaseous fuels. The fact that this type of material can be produced with cheap raw materials is an added advantage. Leion et al. [123] investigated the CLOU behaviour and reactivity of a series of materials of general composition $CaMn_xTi_{1-x}O_3$ with CH_4 in a TGA. Based on the oxygen capacity and the reactivity, the oxygen carrier of $CaMn_{0.875}Ti_{0.125}O_3$ was chosen for further testing with CH_4 and petroleum coke. The reactivity with petroleum coke at 900°C and 950°C was slower compared to previous experiments with Cu-based oxygen carrier [68], which was explained by the slower rate of oxygen uncoupling in this material. Rydén et al. investigated the same material in a 300 W continuously circulating reactor using natural gas [75]. The material exhibited very smooth fluidization behaviour for over 70 h at hot conditions. The uncoupling effect was dependent upon the oxygen concentration in the air reactor, with a higher concentration of O_2 from the fuel reactor as the oxygen concentration was increased in the air reactor. It was possible to achieve complete fuel conversion at 950°C. More recently, Källen et al. investigated the performance of $CaMn_{0.9}Mg_{0.1}O_{3-\delta}$, in a 10 kW natural gas-fired CLC unit [124]. The results showed high rate of oxygen release and full conversion of natural gas—a behaviour superior to that of NiO-based oxygen carrier in the same unit [36, 37].

Arjmand et al. investigated a series of La-doped calcium manganates with gaseous and solid fuels [125]. Six materials of general formula $Ca_xLa_{1-x}Mn_{1-y}M_yO_3$ (M = Ti, Mg, Fe, Cu) were investigated with a 10% substitution of Ca with La and Mn with the metals above. With the exception of the Cu-doped material, it was found that the materials had excellent mechanical strength, CLOU properties, reactivity, and fluidization properties. It appears, however, that the pure $CaMnO_3$ has a higher rate of reaction than all of the doped materials.

Calcium manganate can be produced with very cheap material, that is, CaO and manganese ore [117]. This is likely a very important aspect for solid fuel combustion, as the lifetime of particles in a solid fuel combustor is likely to be much lower than in a gas-fired unit due to deactivation with ash as well as loss of material with the ash flows. The highly promising results from testing of these materials clearly make this one of the more promising combined oxides. However, the effect of sulphur on the particle reactivity and stability needs to be investigated.

4. Kinetics of Oxidation and Reduction of Oxygen Carriers in CLOU

There are only a few studies which have focused on determining the kinetics of the oxygen release and oxidation rates of oxygen carriers for CLOU applications. The focus has been on Cu-based oxygen carriers. Determination of kinetics of CLOU materials poses some additional challenges in comparison to kinetic data of regular CLC materials, as the rate of both the reverse and forward of reaction (5) is a function of an oxygen driving force, given by the difference between the actual oxygen partial pressure and the equilibrium partial pressure of oxygen [102]. In the fuel reactor the release rate, r_d (kg O_2/kg OC,s), of oxygen, or decomposition of CuO, can be expressed generally as

$$r_d = k_r \left(\frac{p_{O_2,\mathrm{eq}} - p_{O_2}}{p_{O_2,\mathrm{eq}}} \right), \qquad (18)$$

where $p_{O_2,\mathrm{eq}}$ is the equilibrium partial pressure of O_2 and k_r is a reaction rate constant. In the fuel reactor, the oxygen concentration should be kept very low at optimized conditions, that is, $p_{O_2} = 0$. Thus, the rate is directly proportional to a reaction rate constant and the equilibrium partial pressure, which is why it is an advantage to have as high temperature in the fuel reactor as possible.

The rate of decomposition can be evaluated in several ways. Arjmand et al. [71] introduced an excess of devolatilized wood char to a bed of freeze-granulated $CuO/MgAl_2O_4$ particles and in this way was able to calculate the rate of decomposition in the temperature interval of 850–900°C. The decomposition reaction was modelled using the Avrami-Erofeev mechanism and the kinetic data were obtained using an Arrhenius expression. From the analysis, an activation energy of 139.3 kJ/mol was calculated for the decomposition reaction. A similar methodology was used by Adanez-Rubio et al. [95], who studied the rate of decomposition from a similar type of oxygen carrier, albeit produced with spray drying. By utilizing small enough ratios of OC/fuel, the maximum rate of oxygen release was obtained as 2.3×10^{-3} kg O_2/kg OC,s at a temperature of approximately 980°C. Whitty and Clayton [102] performed decomposition experiments in three types of reactor systems using N_2 and found that the rates of decomposition were similar independent of reactor type and also very similar for the three Cu-based oxygen carriers evaluated, with an average activation energy found of 110 kJ/moL. Eyring et al. [77] investigated the rate of decomposition of fine CuO in a TGA in the temperature range of 750–950°C, found that the decomposition could be explained by an Arrhenius type of expression, and calculated an activation energy of 327 kJ/mol for the decomposition reaction, which was very similar to that found previously by Chadda et al. [126]. A somewhat smaller activation energy of 281 kJ/mol was obtained by Sahir et al. [127] for the decomposition reaction of a freeze-granulated CuO/ZrO_2 oxygen carrier.

One study has investigated the rate of decomposition of calcium manganate materials. Arjmand et al. [125] employed the same methodology as described above for obtaining the rate of oxygen release from $CuO/MgAl_2O_4$ to evaluate the oxygen release rate from a series of perovskite materials of general formula $Ca_xLa_{1-x}Mn_{1-y}M_yO_3$. The maximum rates of uncoupling were approximately 0.0003–0.0004 kg O_2/kg OC,s at 950°C, which is about 15 times slower than for the earlier investigated Cu-based oxygen carrier at 900°C [71].

A few publications have reported on kinetics of the oxidation reaction, that is, reverse of reaction (5). The general rate expression for the oxidation reaction is given by

$$r_o = k_o \left(p_{O_2} - p_{O_2,\text{eq}} \right), \quad (19)$$

where r_o (kg O_2/kg OC,s) is the rate of the oxidation and k_o is a reaction rate constant. From (19) it is clear that a higher temperature would reduce the driving force for the reaction, that is, $p_{O_2} - p_{O_2,\text{eq}}$, and thus a slower rate of reaction may be expected as the temperature increases. Arjmand et al. [71] also investigated the oxidation rate of the freeze-granulated oxygen carrier of $CuO/MgAl_2O_4$ in the temperature interval of 850–950°C using a batch fluidized bed reactor. The reaction was very fast and the authors were unable to obtain a rate which was not limited by the supply of oxygen to the reactor. Whitty and Clayton investigated the rate of oxidation for an oxygen carrier of CuO/ZrO_2 as a function of temperature and oxygen driving force. Although an increase in oxidation was seen when the oxygen partial pressure was increased, the increase in rate was not as high as expected, indicating that there were other mechanisms restricting oxidation, which is an observation in conformity with previous studies [102]. An activation energy of the oxidation of 202 kJ/mol was found for this oxygen carrier. Eyring et al. also found a decrease in oxidation rate as a function of temperature in the interval of 850–950°C when oxidizing a fine CuO powder in air [77]. Sahir et al. analyzed oxidation data of freeze-granulated particles of CuO/ZrO_2 using the law of additive reaction times and apparent rate constants were determined at 900 and 950°C [127].

5. Design Criteria

In a chemical-looping combustion system, two key design parameters are (i) the solid inventory of oxygen carrier particles in the air and fuel reactor and (ii) recirculation rate of oxygen carrier particles between the interconnected air and fuel reactors. Numerous studies in the literature have calculated these parameters for both gaseous and solid fuel applications, for example, [54, 60, 106, 128]. In a similar way, these values for solid inventory can be calculated for a CLOU process, and this is described below.

The minimum solid inventory, $m_{\text{oc,fr}}$ (kg/MW), for a CLOU process designed with interconnect fluidized bed reactors is related to the oxygen demanded by the fuel and the oxygen release rate from the oxygen carrier material [71, 95],

$$m_{\text{oc,fr}} = \frac{\dot{m}_{\text{O}}}{r_d}. \quad (20)$$

Here, r_d is the rate of oxygen release from the decomposition reaction (kg O_2/kg OC,s) and $\dot{m}_{\text{O}}$ is the rate of oxygen demand by the fuel, with units kg O_2/s, MW.

The circulation rate of the oxygen carrier particles, $\dot{m}_{\text{OC}}$ (kg OC/MW,s), can be calculated from the oxygen demand of the fuel and the change in the degree of mass-based conversion of the solids in the air and fuel reactor, $\Delta\omega$,

$$\dot{m}_{\text{OC}} = \frac{\dot{m}_{\text{O}}}{\Delta\omega}. \quad (21)$$

The amount of oxygen carrier needed in the air reactor can be calculated in a similar way; see Arjmand et al. [71].

Several studies have calculated the mass inventories needed in the fuel reactor of a CLOU system utilizing solid fuels [69, 71, 77, 95, 96]. Adanez-Rubio performed studies of a spray-dried Cu-based material composed of 60 wt% CuO on $MgAl_2O_4$ as inert [95]. Here, the release rate of oxygen was determined by varying the OC/coal ratio. At high OC/coal ratios, there was complete combustion to CO_2, but with excess O_2 in the flue gases. As the OC/fuel ratio was lowered, the oxygen concentration dropped to zero, and the maximum rate of oxygen release from the oxygen carrier was obtained. From these data, the minimum oxygen carrier inventory in the fuel reactor was established to be in the range of 29–39 kg/MW in the temperature range of 930–980°C, although somewhat higher values were suggested in order to achieve complete conversion of CO. In a study by Arjmand et al. [71], a similar methodology and oxygen carrier were employed to obtain reaction kinetics of the oxidation and reduction reaction, and from this data, a total solids inventory of 73–147 kg/MW was calculated assuming char as the fuel.

Experiments in continuous CLOU units employing CuO oxygen carriers have been performed utilizing gaseous, liquid, and solid fuels. Abad et al. [69] performed experiments in a continuously circulating CLOU reactor with bituminous coal and found complete conversion to carbon dioxide using 235 kg/MW of a Cu-based oxygen carrier in the fuel reactor. Adanez-Rubio et al. tested four types of solid fuels in a continuous CLOU unit and from the analysis it was found that between 45 and 490 kg/MW material was needed in the fuel reactor in order to achieve 95% carbon capture [96]. Moldenhauer et al. [31] investigated the combustion of kerosene utilizing CLOU and a CuO/ZrO_2 oxygen carrier in a circulating CLOU unit. The fuel conversion to CO_2 and H_2O was between 95% and 99.99% in the temperature range of 750–900°C. These results were obtained using a total solids inventory (air reactor + fuel reactor + particle locks) corresponding to 2000 kg/MW. However, it is expected that less than half of the oxygen carrier particles were in the fuel reactor. Finally, CLOU has also been tested with natural gas in a 10 kW circulating unit. Källen et al. [124] used the oxygen carrier $CaMn_{0.9}Mg_{0.1}O_3$ for an extensive period of time, that is, 350 h at hot conditions, whereof 55 h with natural gas, and was able to achieve full gas conversion to carbon dioxide at 930°C using a bed mass in the fuel reactor corresponding to 760 kg/MW.

6. Outlook

Chemical-looping combustion (CLC) and chemical-looping with oxygen uncoupling (CLOU) are new processes for oxidizing a fuel. The main advantage with these technologies is that inherent capture of CO_2 is possible with no gas separation step needed in order to obtain the carbon dioxide in pure form. Most research in the last two decades has focused on CLC with gaseous fuels [40], and although there are no commercial units available today, there are a significant number of smaller units in the size range of 0.3–140 kW which have been operated successfully with a wide variety of oxygen carrier materials. It is clear from the operational experience with gaseous fuel that almost complete gas conversion is possible with 100%CO_2 capture. There are today plans of constructing larger natural gas-fired CLC pilots for steam production [129].

Although most research around CLC and CLOU has been conducted with gaseous fuels, it is likely that the greatest advantage with chemical-looping will be realized for power production from solid fuels [130]. This is because these combustion processes are normally conducted at atmospheric pressure and integrated with a Clausius-Rankine steam cycle, which is also what is envisaged with CLC and CLOU with solid fuels. Efficient power production from gaseous fuels would likely require a pressurized process, and there is very little research currently on chemical-looping under pressurized conditions. Despite the technoeconomic promise of CLC with solid fuels, the technology is not without drawbacks. The slow gasification of solid char, reactions (3) and (4), in the fuel reactor will mean that long residence times may be needed in the fuel reactor in order for the fuel to be fully converted to gas. Although most studies report on carbon capture efficiencies in the order of 90%, Markström et al. achieved 99% carbon capture utilizing ilmenite and a bituminous coal in a 100 kW CLC unit [64]. The biggest challenge with normal CLC with solid fuels is likely to achieve a high degree of gas conversion in the fuel reactor. The reactive gases generated from the gasification reactions are generated inside the entire fuel reactor, and some of the gases will not have sufficient contact with oxygen carrier materials, and thus it is expected that even in a well-designed fuel reactor, some small amounts of CO and H_2 will be present at the outlet. Most studies report on gas conversion to carbon dioxide of less than 95%, although there are studies claiming higher degrees of gas conversion. The presence of CO and H_2 in the outlet of the fuel reactor will mean that there may need to be a treatment step downstream of the fuel reactor, which will add to cost and complexity.

The use of CLOU will solve many of the disadvantages with regular CLC. There are no gasification steps, but rather the fuel is burnt with oxygen. The overall char conversion reaction has been shown in several studies to be much faster utilizing Cu-based CLOU particles compared to the rate with a non-CLOU oxygen carrier. For CLOU the uncoupling reactions occur in the emulsion phase where the char and reactive gases are also present and it is believed that it is possible to get full gas conversion even when the mixing is not perfect. Experimental investigations in circulating units give support of this idea. Complete combustion has been obtained in two studies using different types of coal in a circulating CLOU reactor [69, 96]. It can also be speculated that CLOU oxygen carriers will be an advantage using gaseous and liquid fuels. If oxygen is released in the gas phase in regions of low combustibles, this oxygen can be used downstream in the reactor, or freeboard, to convert combustibles which have bypassed the bed. Experimental results from continuous units are promising. All data from continuous units with these types of fuels report very high or complete conversion of the fuel to CO_2 and H_2O [31, 75, 114, 124].

The majority of investigations in the open literature with respect to chemical-looping are devoted to normal CLC, and there are still only a few research groups specifically working on developing oxygen carriers which release oxygen in the gas phase. The focus has been on developing and testing copper oxide-based materials, as is seen in Table 3. The disadvantage with CuO is the high cost, relatively low melting temperature, and the lack of mechanical stability, as several papers report on high rates of attrition or fragmentation. There are certainly some interesting combined oxide systems which may have the advantage that they are less expensive than the Cu-based materials; however, also many studies have reported problems with attrition and fragmentation, especially for the Fe-Mn systems. It is expected that the future trend in research around CLOU materials involves

(i) more tests of promising materials in continuous reactors for extended periods of time,

(ii) investigation of the effect of impurities on oxygen carrier reactivity and stability, most importantly the effects of ash contamination and sulfur poisoning,

(iii) fundamental studies of attrition phenomena for Cu-based and combined metal oxide systems,

(iv) theoretical exploration of additional combined oxide systems which may have properties suitable for the CLOU process.

7. Conclusions

Chemical-looping with oxygen uncoupling (CLOU) is a new and promising method for oxidizing a fuel to carbon dioxide and steam. The process is similar to chemical-looping combustion (CLC) and CO_2 and H_2O are inherently isolated from the rest of the flue gases without the need for an energy intensive gas separation step. The difference between CLC and CLOU is the mechanism for oxidation of the fuel in the fuel reactor. In CLOU the oxygen carrier releases oxygen in the gas phase, which then reacts with the fuel through normal combustion, in contrast to CLC, where the oxygen carrier reacts directly or indirectly with the fuel through a noncatalytic gas-solid reaction. This paper gives a complete overview of the CLOU process and the experimental investigations which have been performed in the last five years. The process has been tested in continuous working CLOU reactors for gaseous, liquid, and solid fuels, with very promising results with respect to rates of fuel conversion. The main advantage with the CLOU process is certainly for solid fuels, but it is suggested that it may also be advantageous with respect to gaseous and liquid fuels.

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References

[1] M. Ishida and H. Jin, "A novel combustor based on chemical-looping reactions and its reaction kinetics," *Journal of Chemical Engineering of Japan*, vol. 27, no. 3, pp. 296–301, 1994.

[2] A. Lyngfelt, B. Leckner, and T. Mattisson, "A fluidized-bed combustion process with inherent CO_2 separation; application of chemical-looping combustion," *Chemical Engineering Science*, vol. 56, no. 10, pp. 3101–3113, 2001.

[3] R. K. Lyon and J. A. Cole, "Unmixed combustion: an alternative to fire," *Combustion and Flame*, vol. 121, no. 1-2, pp. 249–261, 2000.

[4] H. Richter and K. Knocke, "Reversibility of combustion processes," *ACS Symposium Series*, vol. 235, pp. 71–86, 1983.

[5] E. Jerndal, T. Mattisson, and A. Lyngfelt, "Thermal analysis of chemical-looping combustion," *Chemical Engineering Research and Design A*, vol. 84, no. 9, pp. 795–806, 2006.

[6] W. K. Lewis, E. R. Gilliland, and M. P. Sweeney, "Gasification of carbon: metal oxides in a fluidized powder bed," *Chemical Engineering Progress*, vol. 47, pp. 251–256, 1951.

[7] M. Ishida and H. Jin, "A new advanced power-generation system using chemical-looping combustion," *Energy*, vol. 19, no. 4, pp. 415–422, 1994.

[8] M. Ishida and H. Jin, "A novel chemical-looping combustor without NOx formation," *Industrial and Engineering Chemistry Research*, vol. 35, no. 7, pp. 2469–2472, 1996.

[9] M. Ishida and H. Jin, "CO_2 recovery in a power plant with chemical looping combustion," *Energy Conversion and Management*, vol. 38, no. 1, pp. S187–S192, 1997.

[10] M. Ishida, H. Jin, and T. Okamoto, "A fundamental study of a new kind of medium material for chemical-looping combustion," *Energy & Fuels*, vol. 10, no. 4, pp. 958–963, 1996.

[11] M. Ishida, H. Jin, and T. Okamoto, "Kinetic behavior of solid particle in chemical-looping combustion: suppressing carbon deposition in reduction," *Energy & Fuels*, vol. 12, no. 2, pp. 223–229, 1998.

[12] E. Johansson, A. Lyngfelt, T. Mattisson, and F. Johnsson, "Gas leakage measurements in a cold model of an interconnected fluidized bed for chemical-looping combustion," *Powder Technology*, vol. 134, no. 3, pp. 210–217, 2003.

[13] T. Mattisson, A. Järdnäs, and A. Lyngfelt, "Reactivity of some metal oxides supported on alumina with alternating methane and oxygen—application for chemical-looping combustion," *Energy & Fuels*, vol. 17, no. 3, pp. 643–651, 2003.

[14] T. Mattisson, A. Lyngfelt, and P. Cho, "The use of iron oxide as an oxygen carrier in chemical-looping combustion of methane with inherent separation of CO_2," *Fuel*, vol. 80, no. 13, pp. 1953–1962, 2001.

[15] J. Adanez, L. F. de Diego, F. Garcia-Labiano, P. Gayan, A. Abad, and J. M. Palacios, "Selection of oxygen carriers for chemical-looping combustion," *Energy & Fuels*, vol. 18, no. 2, pp. 371–377, 2004.

[16] L. F. de Diego, F. García-Labiano, J. Adánez et al., "Development of Cu-based oxygen carriers for chemical-looping combustion," *Fuel*, vol. 83, no. 13, pp. 1749–1757, 2004.

[17] F. Garcia-Labiano, L. de Diego, J. Adanez, A. Abad, and P. Gayan, "Reduction and oxidation kinetics of a copper-based oxygen carrier prepared by impregnation for chemical-looping combustion," *Industrial and Engineering Chemistry Research*, vol. 43, no. 26, pp. 8168–8177, 2004.

[18] F. García-Labiano, L. F. de Diego, J. Adánez, A. Abad, and P. Gayán, "Temperature variations in the oxygen carrier particles during their reduction and oxidation in a chemical-looping combustion system," *Chemical Engineering Science*, vol. 60, no. 3, pp. 851–862, 2005.

[19] B. Kronberger, E. Johansson, G. Löffer, T. Mattisson, A. Lyngfelt, and H. Hofbauer, "A two-compartment fluidized bed reactor for CO_2 capture by chemical-looping combustion," *Chemical Engineering and Technology*, vol. 27, no. 12, pp. 1318–1326, 2004.

[20] B. Kronberger, G. Löffler, and H. Hofbauer, "Simulation of mass and energy balances of a chemical-looping system," *International Journal of Energy for a Clean Environment*, vol. 6, no. 1, pp. 1–14, 2005.

[21] B. Kronberger, A. Lyngfelt, G. Löffler, and H. Hofbauer, "Design and fluid dynamic analysis of a bench-scale combustion system with CO_2 separation-chemical-looping combustion," *Industrial & Engineering Chemistry Research*, vol. 44, pp. 546–556, 2005.

[22] H. Ryu, D. Bae, and G. Jin, "Carbon deposition characteristics of NiO based oxygen carrier particles for chemical-looping combustor," in *Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies*, J. Gale and Y. Kaya, Eds., pp. 175–180, Elsevier, Oxford, UK, 2002.

[23] H. Ryu, D. Bae, K. Han, S. Lee, G. Jin, and J. Choi, "Oxidation and reduction characteristics of oxygen carrier particles and reaction kinetics by unreacted core model," *Korean Journal of Chemical Engineering*, vol. 18, no. 6, pp. 831–837, 2001.

[24] H. Ryu, D. Bae, and G. Jin, "Effect of temperature on reduction reactivity of oxygen carrier particles in a fixed bed chemical-looping combustor," *Korean Journal of Chemical Engineering*, vol. 20, no. 5, pp. 960–966, 2003.

[25] H. J. Ryu, D. H. Bae, S. H. Jo, and G. T. Jin, "Reaction characteristics of Ni and NiO based oxygen carrier particles for chemical-looping combustor," *Korean Chemical Engineering Research*, vol. 42, pp. 107–114, 2004.

[26] Ö. Brandvoll, L. Kolbeinsen, N. Olsen, and O. Bolland, "Chemical looping combustion-reduction of NiO:$NiAl_2O_4$ with hydrogen," *Chemical Engineering Transactions*, vol. 3, pp. 105–110, 2003.

[27] J. Wolf, M. Anheden, and J. Yan, "Comparison of nickel- and iron-based oxygen carriers in chemical looping combustion for CO_2 capture in power generation," *Fuel*, vol. 84, no. 7-8, pp. 993–1006, 2005.

[28] A. Abad, T. Mattisson, A. Lyngfelt, and M. Johansson, "The use of iron oxide as oxygen carrier in a chemical-looping reactor," *Fuel*, vol. 86, no. 7-8, pp. 1021–1035, 2007.

[29] T. Pröll, K. Mayer, J. Bolhar-Nordenkampf et al., "Natural minerals as oxygen carriers for chemical looping combustion in a dual circulating fluidized bed system," *Energy Procedia*, vol. 1, pp. 27–34, 2009.

[30] A. Abad, T. Mattisson, A. Lyngfelt, and M. Rydén, "Chemical-looping combustion in a 300 W continuously operating reactor system using a manganese-based oxygen carrier," *Fuel*, vol. 85, no. 9, pp. 1174–1185, 2006.

[31] P. Moldenhauer, M. Rydén, T. Mattisson, and A. Lyngfelt, "Chemical-looping combustion and chemical-looping with oxygen uncoupling of kerosene with Mn- and Cu-based oxygen carriers in a circulating fluidized-bed 300W laboratory reactor," *Fuel Processing Technology*, vol. 104, pp. 378–389, 2012.

[32] J. Adánez, P. Gayán, J. Celaya, L. F. de Diego, F. García-Labiano, and A. Abad, "Chemical looping combustion in a 10 kWth prototype using a CuO/Al_2O_3 oxygen carrier: effect of operating conditions on methane combustion," *Industrial and Engineering Chemistry Research*, vol. 45, no. 17, pp. 6075–6080, 2006.

[33] J. Adánez, C. Dueso, L. F. de Diego, F. García-Labiano, P. Gayán, and A. Abad, "Effect of fuel gas composition in chemical-looping combustion with Ni-based oxygen carriers. 2. Fate of light hydrocarbons," *Industrial and Engineering Chemistry Research*, vol. 48, no. 5, pp. 2509–2518, 2009.

[34] F. García-Labiano, L. F. de Diego, P. Gayán, J. Adánez, A. Abad, and C. Dueso, "Effect of fuel gas composition in chemical-looping combustion with Ni-based oxygen carriers. 1. fate of sulfur," *Industrial and Engineering Chemistry Research*, vol. 48, no. 5, pp. 2499–2508, 2009.

[35] P. Kolbitsch, J. Bolhar-Nordenkampf, T. Pröll, and H. Hofbauer, "Operating experience with chemical looping combustion in a 120 kW dual circulating fluidized bed (DCFB) unit," *International Journal of Greenhouse Gas Control*, vol. 4, no. 2, pp. 180–185, 2010.

[36] C. Linderholm, A. Abad, T. Mattisson, and A. Lyngfelt, "160 h of chemical-looping combustion in a 10 kW reactor system with a NiO-based oxygen carrier," *International Journal of Greenhouse Gas Control*, vol. 2, no. 4, pp. 520–530, 2008.

[37] C. Linderholm, T. Mattisson, and A. Lyngfelt, "Long-term integrity testing of spray-dried particles in a 10-kW chemical-looping combustor using natural gas as fuel," *Fuel*, vol. 88, no. 11, pp. 2083–2096, 2009.

[38] L. Fan, *Chemical-Looping Systems for Fossil Energy Conversions*, John Wiley and Sons, Hoboken, NJ, USA, 2010.

[39] A. Lyngfelt, "Oxygen carriers for chemical looping combustion —4000 h of operational experience," *Oil and Gas Science and Technology*, vol. 66, no. 2, pp. 161–172, 2011.

[40] J. Adanez, A. Abad, F. Garcia-Labiano, P. Gayan, and L. F. de Diego, "Progress in chemical-looping combustion and reforming technologies," *Progress in Energy and Combustion Science*, vol. 38, no. 2, pp. 215–282, 2012.

[41] A. Lyngfelt, M. Johansson, and T. Mattisson, "Chemical-looping combustion—status of development," in *Proceedings of the 9th International Conference on Circulating Fluidized Bed (CFB-9 '08)*, Hamburg, Germany, 2008.

[42] M. M. Hossain and H. I. de Lasa, "Chemical-looping combustion (CLC) for inherent CO_2 separations—a review," *Chemical Engineering Science*, vol. 63, no. 18, pp. 4433–4451, 2008.

[43] H. Fang, L. Haibin, and Z. Zengli, "Advancements in development of chemical-looping combustion: a review," *International Journal of Chemical Engineering*, vol. 2009, Article ID 710515, 16 pages, 2009.

[44] E. Johansson, T. Mattisson, A. Lyngfelt, and H. Thunman, "Combustion of syngas and natural gas in a 300 W chemical-looping combustor," *Chemical Engineering Research and Design A*, vol. 84, no. 9, pp. 819–827, 2006.

[45] P. Kolbitsch, J. Bolhàr-Nordenkampf, T. Pröll, and H. Hofbauer, "Comparison of two Ni-based oxygen carriers for chemical looping combustion of natural gas in 140 kw continuous looping operation," *Industrial and Engineering Chemistry Research*, vol. 48, no. 11, pp. 5542–5547, 2009.

[46] P. Pimenidou, G. Rickett, V. Dupont, and M. Twigg, "High purity H_2 by sorption-enhanced chemical looping reforming of waste cooking oil in a packed bed reactor," *Bioresource Technology*, vol. 101, no. 23, pp. 9279–9286, 2010.

[47] Y. CaO, B. Lia, H. Y. Zhao, C. W. Lin, S. Sit, and W. P. Pan, "Investigation of asphalt (Bitumen)-fuelled chemical looping combustion using durable copper-based oxygen carrier," *Energy Procedia*, vol. 4, pp. 457–464, 2011.

[48] A. Hoteit, A. Forret, W. Pelletant, J. Roesler, and T. Gauthier, "Chemical looping combustion with different types of liquid fuels," *Oil & Gas Science and Technology*, vol. 66, pp. 193–199, 2011.

[49] P. Moldenhauer, M. Rydén, T. Mattisson, and A. Lyngfelt, "Chemical-looping combustion and chemical-looping reforming of kerosene in a circulating fluidized-bed 300W laboratory reactor," *International Journal of Greenhouse Gas Control*, vol. 9, pp. 1–9, 2012.

[50] A. Lyngfelt, "Chemical-looping combustion of solid fuels-status of development," in *Proceedings of the 2nd International Conference on Chemical-Looping*, Darmstadt, Germany, 2012.

[51] T. Mattisson, M. Johansson, and A. Lyngfelt, "CO_2 capture from coal combustion using chemical-looping combustion—reactivity investigation of Fe, Ni and Mn based oxygen carriers using syngas," in *Proceedings of the Clearwater Coal Conference*, Clearwater, Fla, USA, 2006.

[52] T. Mattisson, F. García-Labiano, B. Kronberger, A. Lyngfelt, J. Adánez, and H. Hofbauer, "Chemical-looping combustion using syngas as fuel," *International Journal of Greenhouse Gas Control*, vol. 1, no. 2, pp. 158–169, 2007.

[53] N. Berguerand and A. Lyngfelt, "Design and operation of a 10 kWth chemical-looping combustor for solid fuels—testing with South African coal," *Fuel*, vol. 87, no. 12, pp. 2713–2726, 2008.

[54] H. Leion, T. Mattisson, and A. Lyngfelt, "The use of petroleum coke as fuel in chemical-looping combustion," *Fuel*, vol. 86, no. 12-13, pp. 1947–1958, 2007.

[55] S. Scott, J. Dennis, A. Hayhurst, and T. Brown, "In situ gasification of a solid fuel and CO_2 separation using chemical looping," *AIChE Journal*, vol. 52, no. 9, pp. 3325–3328, 2006.

[56] T. Mattisson, A. Lyngfelt, M. Rydén, and H. Leion, "Oxygen carriers for chemical-looping combustion of solid fuels," in *Proceedings of the AiChE Annual Meeting*, Pittsburgh, Pa, USA, 2012.

[57] Y. Cao, B. Casenas, and W. Pan, "Investigation of chemical looping combustion by solid fuels. 2. Redox reaction kinetics and product characterization with coal, biomass, and solid waste as solid fuels and CuO as an oxygen carrier," *Energy & Fuels*, vol. 20, no. 5, pp. 1845–1854, 2006.

[58] J. S. Dennis, C. R. Müller, and S. A. Scott, "In situ gasification and CO_2 separation using chemical looping with a Cu-based oxygen carrier: performance with bituminous coals," *Fuel*, vol. 89, no. 9, pp. 2353–2364, 2010.

[59] A. Cuadrat, A. Abad, L. de Diego, F. García-Labiano, P. Gayán, and J. Adánez, "Prompt considerations on the design of chemical-Looping Combustion of coal from experimental tests," *Fuel*, vol. 97, pp. 219–232, 2012.

[60] A. Cuadrat, A. Abad, F. García-Labiano, P. Gayán, L. de Diego, and J. Adánez, "Effect of operating conditions in Chemical-Looping Combustion of coal in a 500W th unit," *International Journal of Greenhouse Gas Control*, vol. 6, pp. 153–163, 2012.

[61] P. Markström, A. Lyngfelt, and C. Linderholm, "Chemical-looping combustion in a 100 kW unit for solid fuels," in *Proceedings of the 21st International Conference on Fluidized Bed Combustion*, pp. 285–292, Naples, Italy, 2012.

[62] L. Shen, J. Wu, and J. Xiao, "Experiments on chemical looping combustion of coal with a NiO based oxygen carrier," *Combustion and Flame*, vol. 156, no. 3, pp. 721–728, 2009.

[63] A. Tong, S. Bayham, M. Kathe, L. Zeng, S. Luo, and L. Fan, "Iron-based syngas chemical looping process and coal-direct chemical looping process development at Ohio Stare University," in *Proceedings of the 2nd International Conference on Chemical Looping*, Darmstadt, Germany, 2012.

[64] P. Markström, C. Linderholm, and A. Lyngfelt, "Chemical-looping combustion of solid fuels—design and operation of a 100 kW unit with bituminous coal," *International Journal of Greenhouse Gas Control*. In press.

[65] T. Mattisson, A. Lyngfelt, and H. Leion, "Chemical-looping with oxygen uncoupling for combustion of solid fuels," *International Journal of Greenhouse Gas Control*, vol. 3, no. 1, pp. 11–19, 2009.

[66] A. Lyngfelt and T. Mattisson, "Trestegsförbränning för avskiljning av koldioxid," Patent-och registreringsverket, Sweden, 2005.

[67] H. Leion, T. Mattisson, and A. Lyngfelt, "Combustion of a German lignite using Chemical-Looping with Oxygen Uncoupling (CLOU)," in *Proceedings of the 33rd International Technical Conference on Coal Utilization & Fuel Systems, Clearwater Coal Conference*, Clearwater, Fla, USA, 2008.

[68] T. Mattisson, H. Leion, and A. Lyngfelt, "Chemical-looping with oxygen uncoupling using CuO/ZrO_2 with petroleum coke," *Fuel*, vol. 88, no. 4, pp. 683–690, 2009.

[69] A. Abad, I. Adánez-Rubio, P. Gayán, F. García-Labiano, L. F. de Diego, and J. Adánez, "Demonstration of Chemical-Looping with Oxygen Uncoupling (CLOU) process in a 1.5kWth continuously operating unit using a Cu-based oxygen-carrier," *International Journal of Greenhouse Gas Control*, vol. 6, pp. 189–200, 2012.

[70] M. Arjmand, A. Azad, H. Leion, A. Lyngfelt, and T. Mattisson, "Prospects of Al_2O_3 and $MgAl_2O_4$-supported CuO oxygen carriers in chemical-looping combustion (CLC) and Chemical-Looping with Oxygen Uncoupling (CLOU)," *Energy & Fuels*, vol. 25, no. 11, pp. 5493–5502, 2011.

[71] M. Arjmand, M. Keller, H. Leion, T. Mattisson, and A. Lyngfelt, "Oxygen release and oxidation rates of $MgAl_2O_4$-supported CuO oxygen carrier for chemical-looping with oxygen uncoupling (CLOU)," *Energy & Fuels*, vol. 26, pp. 6528–6539, 2012.

[72] P. Gayán, I. Adánez-Rubio, A. Abad, L. F. de Diego, F. García-Labiano, and J. Adánez, "Development of Cu-based oxygen carriers for Chemical-Looping with Oxygen Uncoupling (CLOU) process," *Fuel*, vol. 96, pp. 226–238, 2012.

[73] M. Rydén, H. Leion, T. Mattisson, and A. Lyngfelt, "Combined oxides as oxygen carrier material for chemical-looping with oxygen uncoupling," in *Proceedings of the 2nd International Conference on Chemical-Looping*, Darmstadt, Germany, 2012.

[74] G. Azimi, M. Rydén, H. Leion, T. Mattisson, and A. Lyngfelt, "$Mn_zFe_{1-z})_yO_x$ combined oxides as oxygen carrier for Chemical-Looping with Oxygen Uncoupling (CLOU)," *AIChE Journal*, vol. 59, pp. 582–588, 2013.

[75] M. Rydén, A. Lyngfelt, and T. Mattisson, "$CaMn_{0.875}Ti_{0.125}O_3$ as oxygen carrier for chemical-looping combustion with oxygen uncoupling (CLOU)-Experiments in a continuously operating fluidized-bed reactor system," *International Journal of Greenhouse Gas Control*, vol. 5, no. 2, pp. 356–366, 2011.

[76] A. Shulman, E. Cleverstam, T. Mattisson, and A. Lyngfelt, "Manganese/iron, manganese/nickel, and manganese/silicon oxides used in Chemical-Looping with Oxygen Uncoupling (CLOU) for combustion of methane," *Energy & Fuels*, vol. 23, no. 10, pp. 5269–5275, 2009.

[77] E. Eyring, G. Konya, J. Lighty, A. Sahir, A. Sarofim, and K. Whitty, "Chemical looping with copper oxide as carrier and coal as fuel," *Oil & Gas Science and Technology*, vol. 66, pp. 209–221, 2011.

[78] A. Sahir, A. Cadore, J. Dansie, N. Tingey, and J. Lighty, "Process analysis of chemical looping with oxygen uncoupling (CLOU) and chemical looping combustion (CLC) for solid fuels," in *Proceedings of the 2nd International Conference on Chemical Looping*, Darmstadt, Germany, 2012.

[79] B. Moghtaderi, "Application of chemical looping concept for air separation at high temperatures," *Energy & Fuels*, vol. 24, no. 1, pp. 190–198, 2010.

[80] Z. Li, T. Zhang, and N. Cai, "Experimental study of O_2-CO_2 production for the oxyfuel combustion using a Co-based oxygen carrier," *Industrial and Engineering Chemistry Research*, vol. 47, no. 19, pp. 7147–7153, 2008.

[81] P. Cho, T. Mattisson, and A. Lyngfelt, "Comparison of iron-, nickel-, copper- and manganese-based oxygen carriers for chemical-looping combustion," *Fuel*, vol. 83, no. 9, pp. 1215–1225, 2004.

[82] S. Y. Chuang, J. S. Dennis, A. N. Hayhurst, and S. A. Scott, "Development and performance of Cu-based oxygen carriers for chemical-looping combustion," *Combustion and Flame*, vol. 154, no. 1-2, pp. 109–121, 2008.

[83] L. F. de Diego, P. Gayán, F. García-Labiano, J. Celaya, A. Abad, and J. Adánez, "Impregnated CuO/Al_2O_3 oxygen carriers for

chemical-looping combustion: avoiding fluidized bed agglomeration," *Energy & Fuels*, vol. 19, no. 5, pp. 1850–1856, 2005.

[84] A. Hoteit, M. K. Chandel, and A. Delebarre, "Nickel- and copper-based oxygen carriers for chemical looping combustion," *Chemical Engineering and Technology*, vol. 32, no. 3, pp. 443–449, 2009.

[85] M. Johansson, T. Mattisson, and A. Lyngfelt, "Comparison of oxygen carriers for chemical-looping combustion of methane rich fuels," in *Proceedings of the 19th International Conference on Fluidized Bed Combustion*, Vienna, Austria, 2006.

[86] Q. Zafar, T. Mattisson, and B. Gevert, "Integrated hydrogen and power production with CO_2 capture using chemical-looping reforming-redox reactivity of particles of CuO, Mn_2O_3, NiO, and Fe_2O_3 using SiO_2 as a support," *Industrial and Engineering Chemistry Research*, vol. 44, no. 10, pp. 3485–3496, 2005.

[87] S. Y. Chuang, J. S. Dennis, A. N. Hayhurst, and S. A. Scott, "Kinetics of the chemical looping oxidation of H_2 by a co-precipitated mixture of CuO and Al_2O_3," *Chemical Engineering Research and Design*, vol. 89, no. 9, pp. 1511–1523, 2011.

[88] M. Arjmand, A. M. Azad, H. Leion, A. Lyngfelt, and T. Mattisson, "Evaluation of $CuAl_2O_4$ as an oxygen carrier in chemical-looping combustion (CLC)," *Industrial and Engineering Chemistry Research*, vol. 51, pp. 13924–13934, 2012.

[89] B. M. Corbella, L. de Diego, F. García-Labiano, J. Adánez, and J. M. Palacios, "Characterization and performance in a multicycle test in a fixed-bed reactor of silica-supported copper oxide as oxygen carrier for chemical-looping combustion of methane," *Energy & Fuels*, vol. 20, no. 1, pp. 148–154, 2006.

[90] B. M. Corbella, L. F. de Diego, F. García-Labiano, J. Adánez, and J. M. Palacios, "The performance in a fixed bed reactor of copper-based oxides on titania as oxygen carriers for chemicel looping combustion of methane," *Energy & Fuels*, vol. 19, no. 2, pp. 433–441, 2005.

[91] F. García-Labiano, J. Adánez, L. F. de Diego, P. Gayán, and A. Abad, "Effect of pressure on the behavior of copper-, iron-, and nickel-based oxygen carriers for chemical-looping combustion," *Energy & Fuels*, vol. 20, no. 1, pp. 26–33, 2006.

[92] Q. Zafar, T. Mattisson, and B. Gevert, "Redox investigation of some oxides of transition-state metals Ni, Cu, Fe, and supported on SiO_2 and $MgAl_2O_4$," *Energy & Fuels*, vol. 20, no. 1, pp. 34–44, 2006.

[93] B. Wang, H. Zhao, Y. Zheng, Z. Liu, R. Yan, and C. Zheng, "Chemical looping combustion of a Chinese anthracite with Fe_2O_3-based and CuO-based oxygen carriers," *Fuel Processing Technology*, vol. 96, pp. 104–115, 2012.

[94] L. F. de Diego, F. García-Labiano, P. Gayán, J. Celaya, J. M. Palacios, and J. Adánez, "Operation of a 10 kWth chemical-looping combustor during 200 h with a CuO-Al_2O_3 oxygen carrier," *Fuel*, vol. 86, no. 7-8, pp. 1036–1045, 2007.

[95] I. Adanez-Rubio, A. Abad, P. Gayan, L. de Diego, F. Garcia-Labiano, and J. Adanez, "Identification of operational regions in the Chemical-Looping with Oxygen Uncoupling (CLOU) process with a Cu-based oxygen carrier," *Fuel*, vol. 102, pp. 634–645, 2012.

[96] I. Adanez-Rubio, A. Abad, P. Gayan, L. de Diego, F. Garcia-Labiano, and J. Adanez, "Performance of CLOU process in the combustion of different types of coal with CO_2 capture," *International Journal of Greenhouse Gas Control*, vol. 12, pp. 430–440, 2013.

[97] I. Adanez-Rubio, P. Gayan, A. Abad, L. de Diego, F. Garcia-Labiano, and J. Adanez, "Evaluation of a spray-dried $CuO/MgAl_2O_4$ oxygen carrier for the chemical looping with oxygen uncoupling process," *Energy & Fuels*, vol. 26, pp. 3069–3081, 2012.

[98] I. Adanez-Rubio, P. Gayan, A. Abad, F. Garcia-Labiano, L. De Diego, and J. Adanez, "CO_2 capture in coal combustion by Chemical-Looping with Oxygen Uncoupling (CLOU) with a Cu-based oxygen carrier," in *Proceedings of the 5th International Conference on Clean Coal Technologies (CCT '11)*, Zaragoza, Spain, 2011.

[99] Q. Imtiaz, A. Kierzkowska, M. Broda, and C. Muller, "Synthesis and performance of Al_2O_3, CeO_2 or $MgAl_2O_4$-supported CuO-based materials for chemical looping with oxygen uncoupling," in *Proceedings of the 2nd International Conference on Chemical Looping*, Darmstadt, Germany, 2012.

[100] Q. Song, W. Liu, C. Bohn et al., "A high performance oxygen storage material for chemical looping processes with CO_2 capture," *Energy and Environmental Science*, vol. 6, pp. 288–298, 2013.

[101] Y. Wen, Z. Li, L. Xu, and N. Cai, "Experimental study of natural Cu ore particles as oxygen carriers in chemical looping with oxygen uncoupling (CLOU)," *Energy Fuels*, vol. 26, pp. 3919–3927, 2012.

[102] K. Whitty and C. Clayton, "Measurement and modeling of kinetics for copper-based chemical looping with oxygen uncoupling," in *Proceedings of the 2nd International Conference on Chemical Looping*, Darmstadt, Germany, 2012.

[103] H. Leion, T. Mattisson, and A. Lyngfelt, "Using Chemical-Looping with Oxygen Uncoupling (CLOU) for combustion of six different solid fuels," *Energy Procedia*, vol. 1, pp. 447–453, 2009.

[104] A. Hedayati, A. M. Azad, M. Rydén, H. Leion, and T. Mattisson, "Evaluation of novel ceria-supported metal oxides as oxygen carriers for chemical-looping combustion," *Industrial & Engineering Chemistry Research*, vol. 51, pp. 12796–12806, 2012.

[105] D. Jing, T. Mattisson, M. Rydén et al., "Innovative oxygen carrier materials for chemical-looping combustion," *Energy Procedia*. In press.

[106] Q. Zafar, A. Abad, T. Mattisson, B. Gevert, and M. Strand, "Reduction and oxidation kinetics of Mn_3O_4/Mg-ZrO_2 oxygen carrier particles for chemical-looping combustion," *Chemical Engineering Science*, vol. 62, no. 23, pp. 6556–6567, 2007.

[107] D. Jing, E. Hermans, H. Leion et al., "Manganese-silica combined oxides as oxygen carrier for chemical-looping combustion," in *Proceedings of the 2nd International Conference on Chemical Looping*, Darmstadt, Germany, 2012.

[108] A. Shulman, E. Cleverstam, T. Mattisson, and A. Lyngfelt, "Chemical-Looping with oxygen uncoupling using Mn/Mg-based oxygen carriers—oxygen release and reactivity with methane," *Fuel*, vol. 90, no. 3, pp. 941–950, 2011.

[109] A. Lyngfelt, T. Mattisson, A. Shulman, and E. Cleverstam, "Nya syrebärare för två- och/eller trestegsförbränning," Patent-och registreringsverket (PRV), Sweden, 2009.

[110] A. Lambert, C. Delquie, I. Clemencon et al., "Synthesis and characterization of bimetallic Fe/Mn oxides for chemical looping combustion," *Energy Procedia*, vol. 1, pp. 375–381, 2009.

[111] G. Azimi, H. Leion, T. Mattisson, and A. Lyngfelt, "Chemical-Looping with oxygen uncoupling using combined Mn-Fe oxides-testing in batch fluidized bed," *Energy Procedia*, vol. 4, pp. 370–377, 2011.

[112] G. Azimi, H. Leion, M. Rydén, T. Mattisson, and A. Lyngfelt, "Investigation of different Mn-Fe oxides as oxygen carrier for

chemical-looping with oxygen uncoupling (CLOU)," *Energy & Fuels*, vol. 27, no. 1, pp. 367–377, 2013.

[113] G. Azimi, H. Leion, M. Rydén, T. Mattisson, and A. Lyngfelt, "Solid fuel conversion of iron manganese oxide as oxygen carrier for chemical-looping with oxygen uncoupling (CLOU)," in *Proceedings of the 2nd International Conference on Chemical Looping*, Darmstadt, Germany, 2012.

[114] M. Rydén, A. Lyngfelt, and T. Mattisson, "Combined manganese/iron oxides as oxygen carrier for chemical-looping combustion with oxygen uncoupling (CLOU) in a circulating fluidized bed reactor system," *Energy Procedia*, vol. 4, pp. 341–348, 2011.

[115] M. Arjmand, H. Leion, A. Lyngfelt, and T. Mattisson, "Use of manganese ore in chemical-looping combustion (CLC)—Effect on steam gasification," *International Journal of Greenhouse Gas Control*, vol. 8, pp. 56–60, 2012.

[116] M. Arjmand, H. Leion, M. Mattisson, and A. Lyngfelt, "Evaluation of different manganese ores as oxygen carrier in Chemical-Looping Combustion (CLC) for solid fuels," in *Proceedings of the 2nd International Conference on Chemical Looping*, Darmstadt, Germany, 2012.

[117] A. Fossdal, E. Bakken, B. A. Øye et al., "Study of inexpensive oxygen carriers for chemical looping combustion," *International Journal of Greenhouse Gas Control*, vol. 5, no. 3, pp. 483–488, 2011.

[118] A. M. Azad, A. Hedayati, M. Rydén, H. Leion, and T. Mattisson, "Examining the Cu-Mn-O spinel system as an oxygen carrier in chemical looping combustion," *Energy Technology*, vol. 1, pp. 59–69, 2013.

[119] J. E. Readman, A. Olafsen, Y. Larring, and R. Blom, "$La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_{3-\delta}$ as a potential oxygen carrier in a chemical looping type reactor, an in-situ powder X-ray diffraction study," *Journal of Materials Chemistry*, vol. 15, no. 19, pp. 1931–1937, 2005.

[120] M. Rydén, A. Lyngfelt, T. Mattisson, D. Chen, A. Holmen, and E. Bjørgum, "Novel oxygen-carrier materials for chemical-looping combustion and chemical-looping reforming; $La_xSr_{1-x}Fe_yCo_{1-y}O_{3-\delta}$ perovskites and mixed-metal oxides of NiO, Fe_2O_3 and Mn_3O_4," *International Journal of Greenhouse Gas Control*, vol. 2, no. 1, pp. 21–36, 2008.

[121] Z. Sarshar, F. Kleitz, and S. Kaliaguine, "Novel oxygen carriers for chemical looping combustion: $La_{1-x}Ce_xBO_3$ (B = Co, Mn) perovskites synthesized by reactive grinding and nanocasting," *Energy and Environmental Science*, vol. 4, no. 10, pp. 4258–4269, 2011.

[122] Z. Sarshar, Z. Sun, D. Zhao, and S. Kaliaguine, "Development of sinter-resistant core-shell $LaMn_xFe_{1-x}O_3@mSiO_2$ oxygen carriers for Chemical Looping Combustion," *Energy Fuels*, vol. 26, pp. 3091–3103, 2012.

[123] H. Leion, Y. Larring, E. Bakken, R. Bredesen, T. Mattisson, and A. Lyngfelt, "Use of $CaMn_{0.875}Ti_{0.125}O_3$ as oxygen carrier in chemical-looping with oxygen uncoupling," *Energy & Fuels*, vol. 23, no. 10, pp. 5276–5283, 2009.

[124] M. Källén, M. Rydén, C. Dueso, T. Mattisson, and A. Lyngfelt, "$CaMn_{0.9}Mg_{0.1}O_{3-\sigma}$ as oxygen carrier in a gas-fired 10 kWth Chemical-Looping Combustion Unit," *submitted*.

[125] M. Arjmand, A. Hedayati, A. M. Azad, H. Leion, M. Ryden, and T. Mattisson, "$Ca_xLa_{1-x}Mn_{1-y}M_yO_{3-\sigma}$ (M = Fe, Ti, Mg, Cu) as oxygen carriers for Chemical-Looping with Oxygen Uncoupling (CLOU)," *Energy & Fuels*, 2013.

[126] D. Chadda, J. D. Ford, and M. A. Fahim, "Chemical energy storage by the reaction cycle CuO/Cu_2O," *International Journal of Energy Research*, vol. 13, no. 1, pp. 63–73, 1989.

[127] A. Sahir, H. Sohn, H. Leion, and J. Lighty, "Rate analysis of Chemical-Looping with Oxygen Uncoupling (CLOU) for solid fuels," *Energy Fuels*, vol. 26, pp. 4395–4404, 2012.

[128] A. Abad, J. Adánez, F. García-Labiano, L. F. de Diego, P. Gayán, and J. Celaya, "Mapping of the range of operational conditions for Cu-, Fe-, and Ni-based oxygen carriers in chemical-looping combustion," *Chemical Engineering Science*, vol. 62, no. 1-2, pp. 533–549, 2007.

[129] S. Sit, A. Reed, U. Hohenwarter, V. Horn, K. Marx, and T. Pröll, "10 MW CLC field pilot," in *Proceedings of the 2nd International Conference on Chemical Looping*, Darmstadt, Germany, 2012.

[130] C. Ekström, F. Schwendig, O. Biede et al., "Techno-economic evaluations and benchmarking of pre-combustion CO_2 capture and oxy-fuel processes developed in the European ENCAP project," *Energy Procedia*, vol. 1, no. 1, pp. 4233–4240, 2009.

[131] S. Mörstedt and G. Hellsten, *Data Och Diagram*, Malmö, Sweden, 2003.

[132] I. Adanez-Rubio, A. Abad, P. Gayan, F. Garcia-Labiano, L. de Diego, and J. Adanez, "The fate of sulphur in the CLOU process using a Cu-based oxygen-carrier," in *Proceedings of the 2nd International Conference on Chemical Looping*, Darmstadt, Germany, 2012.

[133] M. Rydén, C. Linderholm, P. Markström, and A. Lyngfelt, "Release of gas-phase O_2 from ilmenite during chemical-looping combustion," *Chemical Engineering & Technology*, vol. 35, pp. 1968–1972, 2012.

[134] M. Arjmand, H. Leion, T. Mattisson, and A. Lyngfelt, "ZrO_2-supported CuO oxygen carriers for chemical-looping with oxygen uncoupling (CLOU)," *Energy Procedia*. In press.