CHEMICAL-LOOPING COMBUSTION: STATUS AND RESEARCH NEEDS

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Abstract

Chemical-Looping Combustion (CLC) has emerged in recent years as a very promising combustion technology for power plants and industrial applications with inherent CO₂ capture, which circumvent the energy penalty imposed on other competing technologies. The process is based on the use of a metal oxide to transport the oxygen needed for combustion in order to prevent direct contact between the fuel and air. CLC is performed in two interconnected reactors, and the CO₂ separation inherent to the process practically eliminates the energy penalty associated with gas separation. The CLC process was initially developed for gaseous fuels, and its application was subsequently extended to solid fuels. The process has been demonstrated in units of different size, from bench scale to MW-scale pilot plants, burning natural gas, syngas, coal and biomass, and using ores and synthetic materials as oxygen-carriers.

An overview of the status of the process, starting with the fundamentals and considering the main experimental results and characteristics of process performance, is made both for gaseous and solid fuels. Process modelling of the system for solid and gaseous fuels is also analysed. The main research needs and challenges both for gaseous and solid fuel are highlighted.

Keywords: CO₂ capture; Chemical-Looping Combustion.

1. Introduction

Chemical-Looping Combustion (CLC) is an unmixed combustion process based on the transfer of oxygen from the air to a fuel by means of an active metal oxide (M_xO_y), preventing direct contact between fuel and air. CLC is a very promising technology for power plants due to its inherent CO_2 capture, which circumvents the energetic penalty associated with CO_2 or air separation present in other technologies, resulting in low capture costs. The process is typically performed in two reactors or in two steps, as shown in Fig. 1.

Fig. 1. Diagram of the Chemical-Looping Combustion (CLC) process.

The fuel is oxidized to CO_2 and H_2O by an oxygen-carrier, most commonly a metal oxide (M_xO_y), which is reduced to a metal (M) or a reduced form M_xO_{y-1} inside the fuel-reactor according to reaction (R1). After water condensation and purification, a highly concentrated stream of CO_2 ready for transport and storage is achieved. This concept is the main advantage of the process in relation to other CO_2 capture technologies. CO_2 capture is inherent to this process, as the air is not mixed with the fuel, and the energy penalty for the separation is very low. The oxygen-carrier is further oxidized with air inside the air-reactor (AR), and the regenerated material is ready to start a new cycle (R2). The flue gas contains N_2 and unreacted O_2 . The global enthalpy change of the process is the same as that of conventional combustion where the fuel is burned in direct contact with the oxygen in air (R3).

The principle was proposed in a patent by Lewis and Gilliland [1] to produce pure CO₂ from any oxidizable carbonaceous material. The term Chemical-Looping Combustion was coined by Ishida, Zheng and Akebata [2]. The CLC process using interconnected fluidized beds was a paper concept in 2000 and has now reached a development level of TRL 6. An overview of the CLC process can be found in a number of review publications [3-6]. A specific review on CLC with solid fuels was produced by Adánez et al. [7].

CLC was initially developed for gaseous fuels (natural gas, CH₄, syngas) under atmospheric pressure. Different configurations have been proposed to apply the CLC concept to the combustion of gaseous fuels, including the use of two interconnected, moving [8] or fluidized-bed reactors [9], fixed-bed reactors [10], or a rotating reactor [11]. The most used configuration for the fuel-reactor is a fluidized bed either in the bubbling or high-velocity regime, with the air-reactor acting as a riser to drive oxygen-carrier circulation. Also the use of a moving-bed has been also considered in the CLC configuration [6]; see Table 1. The concept of circulation based on two interconnected fluidized beds has several advantages over alternative designs because it provides good mixing of solids and heat transfer management, as well as a high flow of solid material between fuel- and air-reactors.

Table 1. Description of some reactors configuration for selected CLC units (FR: fuel-reactor; AR: air-reactor).

Thermal power	Location	Main characteristics	Reference
120 kW _{th}	Technical University of Vienna (TUWIEN)	- Dual Circulating Fluidized Bed (DCFB) - FR: turbulent regime - AR: fast fluidization	[12]
10 kW _{th}	IFP-France	- One bubbling FR - Two bubbling AR - Three risers for solids circulation	[13]
50 kW _{th}	Korea Institute of Energy Research (KIER)	- FR: bubbling regime - AR: bubbling regime - Two injection nozzles for solids circulation	[14]
150 kW _{th}	SINTEF	-Double loop circulating fluidized-bed - FR and AR: fast fluidization regime	[15]
25 kW _{th}	Ohio State University (OSU)	- FR: moving bed - AR: with a riser for solids circulation	[16]

CLC offers great flexibility in regard to fuel characteristics, making the use of gaseous, liquid and solid fuels feasible. The use of coal in CLC is highly attractive in scenarios with restrictions on CO₂ emissions, given that coal will continue to be a major energy source in the medium-term. In cases where biomass wastes (BECCS) are used as fuel, the captured CO₂ can be considered negative emissions because this CO₂ has been removed from the atmosphere through photosynthesis in the plants.

With respect to the power cycle when burning gaseous fuels, in order to achieve competitive energy efficiencies, it is necessary to operate at high temperatures and high pressures (1-3 MPa) [17]. There are some concerns regarding operation of pressurized interconnected fluidized beds owing to the difficulties in preventing solids entrainment to the gas turbine found with pressurized fluidized-bed combustion boilers. Moreover, deep loop seals combined with active backpressure control must be considered for stable operation. There is little experience in the use of interconnected fluidized-beds for pressurized-CLC [18,19]. Instead, dynamically operated packed-bed reactors have been proposed for the operation of CLC under pressure [10]. The process consists of alternate oxidation and reduction cycles in separate reactors, with a large number of parallel reactors required to assure a continuous gas stream to the downstream gas turbine.

The Chemical-Looping concept can also be applied to hydrogen production through reforming processes of CH₄ in different ways [6], although the focus of this work is on the combustion process.

2. Fundamentals

The cornerstone of Chemical-Looping processes is the oxygen-carrier. The CLC concept is based in the transfer of oxygen from the air to the fuel by means of a solid oxygen-carrier. For a system of two interconnected fluidized beds, there must be a high enough solids circulation between the

reactors to transfer the oxygen necessary for combustion of the fuel and the heat required to maintain the heat balance in the system, if necessary.

2.1. Mass and heat balances

Depending on the oxygen-carrier properties and fuel used, the oxygen-carrier circulation rate between reactors can be calculated by a mass balance. Assuming the full conversion of gas ($\Delta X_f = 1$) for 1 MW_{th} fuel input, the solid circulation rate ($\dot{m}_{oc}$) can be calculated [20].

$$\dot{m}_{oc} = \frac{1}{R_{oc}\Delta X_s} \frac{2dM_o}{\Delta H_c^0} \quad (1)$$

where d is the stoichiometric coefficient for O₂ in reaction (R3), M_o the atomic weight of oxygen, and ΔH_c^0 the standard combustion heat of the fuel. ΔX_s is the difference in conversion of solids between the inlet and the outlet of the fuel- or air-reactors. The solids conversion of the oxygen-carrier is defined as

$$X_s = \frac{m - m_r}{m_o - m_r} = \frac{m - m_r}{R_{oc}m_o} \quad (2)$$

where m is the instantaneous mass and the denominator is the maximum oxygen transport between the fully oxidized, m_o , and reduced, m_r , oxygen-carrier. The oxygen transport capacity of the material, R_{oc} , defined by equation (3), depends on the oxygen transport capability of the oxide, R_o , and the fraction of the active compound for the oxygen transport, x_{oc} .

$$R_{oc} = x_{oc}R_o \quad (3)$$

The oxygen transport capability, R_0 , is dependent on the metal oxide and redox reactions considered. Table 2 shows the R_0 values for some redox systems of interest. Higher R_0 values correspond to CaSO_4 , Co_3O_4 , NiO and CuO . However, the oxygen transport capacity of an oxygen-carrier, R_{OC} , also depends on the fraction of active phase in the material, as the oxygen-carrier is commonly formed by mixing the active phase with an inert phase, which supplies chemical and physical stability to the oxygen-carrier.

Table 2. Values for the oxygen transport capacity of different redox systems.

Redox pair	R_0
CaSO_4/CaS	0.47
$\text{Co}_3\text{O}_4/\text{Co}$	0.27
$\text{Co}_3\text{O}_4/\text{CoO}$	0.067
CuO/Cu	0.20
$\text{Cu}_2\text{O}/\text{CuO}$	0.10
$\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$	0.034
$\text{Fe}_2\text{O}_3/\text{FeO}$	0.10
$\text{Fe}_2\text{TiO}_5/\text{FeTiO}_3$	0.050
$\text{Mn}_2\text{O}_3/\text{MnO}$	0.10
$\text{Mn}_2\text{O}_3/\text{Mn}_3\text{O}_4$	0.034
NiO/Ni	0.21

Oxygen transport capacity, R_{OC} , is one important characteristic of the oxygen-carrier for process design and operation because it is an indicator of the amount of oxygen that can be transferred by the oxygen-carrier between reactors. Thus, the solids circulation rate necessary to fulfil the mass balance increases with decreasing R_{OC} by a lower value of R_0 for the redox pair, or by a lower fraction of the active oxide in the oxygen-carrier. Fig. 2 shows the circulation rates, $\dot{m}_{OC}$, necessary for the combustion of different fuel gases (CH_4 , CO , H_2) as a function of the oxygen transport capacity of the oxygen-carrier, R_{OC} , and of the difference in conversion, ΔX_s , obtained during operation. The differences in $\dot{m}_{OC}$ as a consequence of the fuel gas used are linked to the oxygen needed for the reaction of each fuel gas. Thus, in order to produce 1 MW_{th} , $1.25 \text{ mol CH}_4 \text{ s}^{-1}$, $3.53 \text{ mol CO s}^{-1}$ or $4.14 \text{ mol H}_2 \text{ s}^{-1}$ are necessary as a consequence of their different

combustion enthalpies, together with oxidant flow rates, $\dot{m}_o$, of 80, 56 or 66 g/s of oxygen, respectively. Usually, the ratio between the molar oxygen flow transported by the oxygen-carrier and the stoichiometric amount for complete combustion of the fuel is defined as the oxygen-carrier-to-fuel ratio, ϕ , given by

$$\phi = \frac{R_{OC}\dot{m}_{OC}}{\dot{m}_o M_o} \quad (4)$$

Fig. 2. Circulation rates of oxygen-carrier necessary to fulfil oxygen balance as a function of the oxygen transport capacity (R_{OC}), fuel gas and change in conversion of solids between reactors (ΔX_s) [20].

Circulation rate of solids between reactors is also influenced by the hydrodynamic behaviour, particularly inside the riser, and the heat balance throughout the entire system because the reduction of metal oxide is an endothermic process in some redox systems utilized, and the oxygen-carrier must transfer enthalpy from the air-reactor. The solids circulation rate in circulating fluidized bed (CFB) systems depends on the operating conditions and riser configuration. Abad et al. [20] selected 16 kg/s MW_{th} as the maximum circulation rate feasible in a CLC plant at atmospheric pressure without increased costs, according to commercial experience. An oxygen transport capacity higher than $\approx 0.4\%$ is required to allow full combustion to CO_2 and

H₂O. For NiO/Ni or CuO/Cu, 2 wt% is sufficient owing to their oxygen transport capacity. However, for Mn₃O₄/MnO and Fe₂O₃/Fe₃O₄, values higher than 6 wt% and 12 wt% respectively are needed owing to their low oxygen transport capacity.

2.2. Heat balance

The overall heat release in a CLC system is the same as that of common combustion, although the distribution of enthalpy depends on the fuel gas and the metal oxide redox pair. The oxidation reaction is always exothermic. However, the reduction reaction may be exothermic or endothermic, depending on the redox system. The energy involved during the reduction with CH₄ is significantly different to that involved in the reduction with H₂ or CO. Thus, in most of the redox pairs, the reduction with CH₄ is endothermic, whereas the reduction with H₂ or CO usually is exothermic, and always exothermic for the redox pair CuO/Cu. When the reduction reaction is endothermic, the oxygen-carrier material is used to transport energy from the air-reactor to the fuel-reactor. Thermal integration between the air-reactor and fuel-reactor has consequences on system operation [20].

Depending on the oxygen carrier and operating conditions, it may be necessary to remove heat from the fuel-reactor to avoid an excess of temperature in this reactor. This is especially important for copper, given to its low melting point.

When the reduction is endothermic, the fuel-reactor is heated by the solids circulating coming from the air-reactor and the temperature decreases in the fuel-reactor. To prevent a large temperature drop, the solids circulation rate is increased with a decrease in the conversion of the oxygen-carrier in this reactor. High temperatures in the air-reactor that can lead to the appearance of operational problems through formation of solid agglomerates must also be avoided. Moreover, in order to maintain the energy balance in the system, a fraction of thermal power, about 50-65%, must be removed from the air-reactor.

3. Chemical-Looping of gaseous fuels

3.1. Oxygen-carriers suitable for gaseous fuels

Characteristics of the oxygen-carrier are crucial for the design of the CLC system and its performance. Significant efforts have been made in the field of oxygen-carrier development in recent years. A few redox pairs have the capability to be reduced by fuel gases and regenerated by air under boiler conditions, and at the same time achieve a high selectivity towards CO_2 and H_2O . Thus, most of the oxygen-carriers proposed in the literature as suitable for gas combustion are synthetic materials using oxides of Cu, Fe, Ni or Mn as active material, also including some mixed oxides with a perovskite structure. A selection of oxygen-carrier materials for natural gas and syngas combustion has been summarized by Hossain et al. [3] and Adanez et al. [6].

The main additional cost for CLC with gaseous fuels is oxygen-carrier replacement. These materials must fulfil a number of different criteria in order to be suitable for CLC. Oxygen-carriers need to have sufficient oxygen transport capacity (R_{OC}), with high reactivity both for reduction and oxidation reactions, and this must be maintained over a large number of redox cycles. Oxygen-carriers need to have favourable thermodynamics with regard to fuel conversion to CO_2 and H_2O for CLC, or CO and H_2 for Chemical-Looping Reforming (CLR). Moreover, negligible carbon deposition during reduction is needed to prevent C shortcutting to the air-reactor, which reduces overall CO_2 capture efficiency. Good fluidization properties and no agglomeration in the reactors are fundamental for the smooth operation of interconnected fluidized bed reactors. Environmental and health issues must be considered to ensure the process meets future high standards of environmental performance. In general, nickel and cobalt are considered the materials with the highest risks during operation. On the contrary, iron is considered a non-toxic material. Copper and manganese could present some environmental problems only when in solution as ions. Resistance to attrition is a key point to consider in order to reduce losses of elutriated fines and to reduce oxygen-carrier replacement costs when fluidized bed reactors are used. Crushing strength

and attrition tests, measured at ambient conditions, are only preliminary indicators. It is necessary to consider whether chemical stress caused by redox reactions is present together with the effects of physical attrition during CLC operation. Thus, attrition behaviour measured during CLC operation in a continuous CLC unit is a good indicator of the behaviour to be expected in an industrial CLC system and allows the lifetime of oxygen-carriers to be calculated. However, accurate values of this parameter need to be evaluated at full scale. Table 3 shows the lifetime data available in the literature from long-term testing in continuous units. The greatest experience corresponds to Ni-based and Cu-based oxygen-carriers.

Table 3. Relevant information on the use of oxygen-carrier in CLC units for natural gas.

Oxygen-carrier	Size of unit	Operation time (h)	Temp. (°C)		Attrition rate (%/h)	Lifetime (h)	Ref.
			FR	AR			
NiO/Al ₂ O ₃	10 kW _{th}	100	≈ 900	1000	0.0023	40000	[21]
NiO/NiAl ₂ O ₄ + MgAl ₂ O ₄	10 kW _{th}	1016	≈ 940	1000	0.003	33000	[22]
NiO/NiAl ₂ O ₄	10 kW _{th}	160	≈ 940	1000	0.022	4500	[23]
NiO/α-Al ₂ O ₃	500 W _{th}	70	880	950	0.01	10000	[24]
CuO/γ-Al ₂ O ₃	10 kW _{th}	100	800	800	0.04	2400	[25]
CuO/γ-Al ₂ O ₃	500 W _{th}	60	800	900	0.09	1100	[26]
CuO/NiO-Al ₂ O ₃	500 W _{th}	67	900	950	0.04	2700	[27]
CuO14/γAl ₂ O ₃	500 W _{th}	60	800	850	0.02	5000	[28]
Commercial							
Ca _{0.9} Mg _{0.1} Mn _{0.9} O _{3-δ}	10 kW _{th}	55	900	900	0.0085	12000	[29]
Ca _{0.9} Mg _{0.1} Mn _{0.9} O _{3-δ}	500 W _{th}	54	900	900	0.09	1100	[30]
Fe ₂ O ₃ /Al ₂ O ₃	500 W _{th}	46	950	950	0.09	1100	[31]

Ni-based materials clearly show greater lifetimes. However, other oxygen-carriers are preferred at present because of environmental concerns. Research to produce copper particles that are highly resistant to attrition and chemical degradation gave lifetime values of up to 5000 h [28] for particles impregnated with 14 wt% CuO. Totally different results were found for CaMn_{0.9}Mg_{0.1}O_{3-δ} particles when tested in different units. This was likely due to the change in conversion of the different solids between the reactors used in each experimental unit that affected the chemical

stress to which the oxygen-carrier particles were subjected, which could be similar to that found by Adanez-Rubio et al. [32] during coal combustion using Cu-Mn oxygen-carriers.

The cost of the makeup stream of solids to replace the loss of fines will depend on the lifetime of particles, the inventory in the CLC system and the cost of the oxygen-carrier, which is mainly affected by its reactivity, the metal used in its composition, and the proportion used.

Oxygen-carrier inventories [6] needed to reach complete combustion of fuel vary greatly depending on the oxygen-carrier used, and also on the flow pattern existing in the reactor (bubbling or fast fluidized bed). Different approaches have been used to extrapolate inventories of oxygen-carrier in the fuel- and air-reactors. However, most of them resulted in high levels of uncertainty. In order to provide reliable results, performance data on combustion efficiency as a function of the oxygen-carrier-to-fuel ratio, ϕ , should be determined in continuous units. ϕ is calculated by means of equation (4) as the ratio between the oxygen supplied by the oxygen-carrier and the oxygen needed to stoichiometrically react with the fuel flow. Combustion efficiency is calculated by taking into account the oxygen transferred to the fuel by the oxygen-carrier in relation to the stoichiometric oxygen required to fully convert the fuel to CO₂ and H₂O; see equation (5). The difference between them is linked to inefficiency in fuel combustion. For adequate comparison it is necessary to conduct experiments in units with a similar flow regime in controlled conditions, and with good measurement of ϕ .

$$\text{Combustion efficiency} = \frac{\text{oxygen transferred by oxygen-carrier}}{\text{oxygen demanded by fuel for full combustion}} \quad (5)$$

Fig. 3 shows combustion efficiency vs ϕ obtained in the 500W_{th} unit equipped with a bubbling fluidized bed fuel-reactor at ICB-CSIC using Cu₁₅Ni₃ [27], Ni₁₈Al [24], Ni₁₁CaAl [33], Fe₁₅Al [31] and CaMn_{0.9}Mg_{0.1}O_{3-δ} [30]. Very different oxygen-carrier-to-fuel ratios, with ϕ

values ranging from 1.1 to 12, were needed to achieve complete or near complete combustion efficiency, which had a direct relation on the change in conversion (ΔX_s) of the oxygen-carrier between reactors. Consequently, Ni11CaAl achieved values of 83%, while only an 8% change in conversion was needed for $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$. This indicates the need to operate at very different solids circulation flow rates between the fuel- and air-reactors, although these values can be reached without any difficulty in circulating fluidized reactors.

Fig. 3. Effect of ϕ on the combustion efficiency for different oxygen-carriers in the 500 W_{th} unit.

Significant differences in the inventories ($\text{kg}/\text{MW}_{\text{th}}$) of oxygen-carrier needed to reach complete combustion were found for different oxygen-carriers. These differences were due to differences in oxygen transport capacity, reactivity and type of flow in the reactor. Ni-based oxygen-carriers were the most reactive, followed by Cu-based materials. Inventories combined with attrition data and oxygen-carrier cost can be used to estimate the makeup costs in a CLC system. However, process modelling is necessary for design and optimization purposes.

Gaseous fuels (natural gas, syngas, refinery gas, sour gas) contain differing amounts of sulphur compounds. H_2S can affect the behaviour of some oxygen-carriers depending on the redox pair used. Sulphur fed into the system can react with the oxygen-carrier by poisoning, forming sulphides that probably cause its deactivation, decreasing the reactivity and, therefore, combustion efficiency of the gaseous fuel reached in the fuel-reactor. Thus, in this case, it was necessary to

desulphurize the gas before CLC combustion. This situation affected Ni-based carriers [34] and some Mn-based carriers ($\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$) with a perovskite structure [30]. The poisoning was attributed to the formation of undesired Ni_3S_2 for Ni-based carriers and CaSO_4 and CaS , respectively.

Moreover, sulphur can be released as SO_2 in the air-reactor outlet stream and must comply with legislation restricting SO_2 emissions (35 mg/Nm^3) for power plants, or it can be present in the fuel-reactor outlet, which would affect the quality of the CO_2 and have significant consequences for the compression, transport and storage steps [35].

Fe-based and Cu-based oxygen-carriers were found to offer good performance in CLC when using fuels containing H_2S [36] with most of the sulphur present as SO_2 in the CO_2 stream coming from the fuel-reactor. Cu carriers can be operated at typical H_2S concentrations for natural gas without deactivation. However, for sour gas (0.3 to 15 % vol H_2S), CH_4 and H_2S were completely burnt, although some amounts were also released in the air-reactor. In the case of the Fe-based oxygen-carrier, the presence of H_2S in the fuel gas did not significantly affect the behaviour of the material, regardless of the amount of sulphur present in the fuel stream, with all S present as SO_2 in the fuel-reactor outlet, together with CO_2 .

3.2. Pilot testing for gaseous fuels

Several CLC units for gaseous fuels can be found in the literature, ranging in scale between the 10 kW_{th} units located at Chalmers University of Technology (CUT), Instituto de Carboquímica (ICB-CSIC), IFP-TOTAL and Xi'an Jiangtong University; the 50 kW_{th} units at KIER (Korea) and NTEL Morgantown (USA); and the 120 kW_{th} pilot plant located at the Vienna University of Technology (TUWIEN) [6,37].

Long operation times were successfully conducted in two different 10 kW_{th} prototypes built at CUT and ICB-CSIC. The 10 kW_{th} unit at CUT was operated for more than 1400 h using different Ni-based and Fe-based oxygen-carriers and natural gas as fuel [21,22], in addition to one mixed

oxide with a perovskite structure, $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ [29]. Long-term tests (>1000 h) using Ni-based oxygen-carriers were conducted at 10 kW_{th} at CUT to analyse the integrity of the particles with respect to reactivity and physical characteristics. High fuel conversion (98-99%) was reported.

The 10 kW_{th} unit at ICB-CSIC was operated for 120 h, using a Cu-based oxygen-carrier prepared by impregnation on Al_2O_3 and methane as fuel [25]. Complete methane conversion with 100% selectivity to CO_2 and H_2O was achieved without deactivation or agglomeration. Xi'an Jiaotong University in China [19] reported operation under pressure (0.3 MPa) using $\text{Fe}_2\text{O}_3/\text{CuO}$ burning coke oven gas and reaching a conversion rate of 92.3%. Ni-based carriers and Co-based oxygen-carriers were tested in two different 50 kW_{th} units at the Korea Institute of Energy Research, KIER-1 and 2 [14,38], with natural gas.

A $120\text{ kW}_{\text{th}}$ dual CFB pilot plant of at TUWIEN [12,39-41] was successfully operated using methane and syngas as fuels with two kinds of Ni-based oxygen-carriers, ilmenite, Cu-based and Fe-based carriers. Moreover, mixed oxides with a perovskite structure ($\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ and $\text{CaMn}_{0.775}\text{Mg}_{0.1}\text{Ti}_{0.125}\text{O}_{3-\delta}$) were tested in this unit burning CH_4 and syngas. Near complete CH_4 conversion was obtained, with high ϕ values close to 25 for $\text{CaMn}_{0.775}\text{Mg}_{0.1}\text{Ti}_{0.125}\text{O}_{3-\delta}$ [41]. These high values are needed in order to take advantage of the properties of the material for generating gaseous oxygen when the solids conversion rate is very low.

A 1 MW CLC unit at Darmstadt University of Technology, designed for solid fuel, was also used for CH_4 combustion. For gaseous fuel, the unit was operated with a Mn-based perovskite $\text{CaMn}_{0.775}\text{Mg}_{0.1}\text{Ti}_{0.125}\text{O}_{3-\delta}$ for 50 h, with a gas conversion rate of 80 %.

Although more than 2000 oxygen-carriers have been investigated, only about 15 have been tested in continuous units of different sizes, ranging from $0.3\text{ kW}_{\text{th}}$ to 1 MW_{th} . Most of the experimental work has been performed with NiO, CuO and Fe_2O_3 oxygen-carriers with different metal oxide contents and using different carrier preparation methods and supports. According to results

obtained on combustion efficiency and lifetime, oxygen-carriers based on Ni, Cu, Fe and Mn with a perovskite structure could be selected, with Cu-based and Fe-based oxygen-carriers suitable for fuel gases containing sulphur, while Ni-based and Mn-based perovskites could be suitable for clean fuel gases.

4. CLC with solid fuels

Several design configurations are being considered for solid fuels, with the fuel-reactor in the form of a moving or fluidized-bed, or even with discontinuous operation [7]. Among them, the use of interconnected CFBs is a preferred configuration because it is more flexible, easy to control and scalable. The following presents the main aspects of its use.

4.1. Description of the CLC process with solid fuels

Fig. 4 shows a schematic diagram of the CLC process with solid fuels. The solid fuel is fed into the fuel-reactor and mixed with the oxygen-carrier particles. Most of the experimental results have been achieved in the *in-situ* Gasification Chemical-Looping Combustion (*iG-CLC*) mode, where the fuel conversion follows the scheme shown by reactions (R4)-(R6); see Fig. 5. In *iG-CLC*, the fuel is *in-situ* gasified by steam and/or CO₂ to produce gaseous products that are oxidized by the oxygen-carrier.

Fig. 4. Schematic diagram of CLC with solid fuels [7].

In order to decrease the steam requirements, wet or dry recirculated streams, including a mixture of H₂O+CO₂, can be used as the fluidizing and gasifying agent, but high CO₂ concentrations are only recommended for highly reactive fuels. It should be noted that char conversion must be guaranteed in the fuel-reactor in order to limit the transport of unconverted carbon to the air-reactor, where the oxygen-carrier is regenerated by air, although the presence of carbon will also produce non-captured CO₂. In order to minimize char losses to the air-reactor, a fluidized bed carbon stripper is used to separate the char from the oxygen-carrier by selective entrainment and, therefore, to achieve CO₂ capture efficiencies of up to 99 % [42].

Fig. 5. Main processes involved in fuel-reactor for *iG*-CLC and CLOU.

Complete combustion of volatiles and gasification products is not usually achieved in *iG*-CLC, so an oxygen-polishing step is proposed in order to oxidize unconverted products such as H₂, CO and CH₄. This step consumes high-purity oxygen in order to maintain the benefits of the CO₂ capture by CLC, and it must needs to use the minimum amount of pure oxygen with near complete use of oxygen to avoid adding corrosive gas to the CO₂ stream in presence of H₂O [43]. This issue has not been specifically investigated for CLC.

Alternatively, the Chemical-Looping with Oxygen Uncoupling process (CLOU) process is based on the use of oxygen-carriers which release gaseous oxygen (R7) inside the fuel-reactor, followed by the combustion of volatile matter and char (R8); see Fig. 5 [44]. Char and volatile matter conversion is better in CLOU than in *iG*-CLC [45] because CLOU involves combustion reactions. However, *iG*-CLC is based on the gasification of char followed by combustion of gasification products. Char gasification rates are up to 100 times slower than those of combustion. These facts explain the better performance of CLOU process with respect to *iG*-CLC. Complete combustion in CLOU mode is feasible with low amounts of solids in the fuel-reactor and steam is not required to achieve high CO₂ capture rates, as it is possible to use recirculated CO₂ as the fluidizing agent.

It must be also taken into account that the ash generated during combustion in both *iG*-CLC and CLOU should be periodically purged to prevent accumulation in the CLC system, although this can lead to a certain loss of oxygen-carrier. A makeup flow of oxygen-carrier should also be added to correct this loss and that caused by particle attrition.

4.2. Suitable oxygen-carriers for CLC with solid fuels

Owing to losses of oxygen-carrier during the drainage of fuel ashes, research is mainly focused on *i*G-CLC using low-cost materials as oxygen-carriers. The most commonly used materials are ilmenite, iron ores, manganese ores, and some wastes from the iron industry and red mud ($\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$). Their performance regarding oxygen demand for oxygen polishing is dependent on their reactivity.

However, no natural materials with relevant oxygen uncoupling properties have been identified. Great efforts are being made to develop synthetic materials for CLOU due to their improved combustion performance [46]. The superior performance of CLOU combustion in terms of oxygen demand and CO_2 capture allows the use of more expensive synthetic oxygen-carriers. Oxygen-carriers suitable for the CLOU process must have suitable thermodynamic properties at temperatures of interest, i.e. 800–1200 °C, evolving gaseous oxygen under fuel-reactor conditions, and they must later allow oxidization by air in the air-reactor. Three metal oxide systems have so far been identified: $\text{CuO}/\text{Cu}_2\text{O}$, $\text{Mn}_2\text{O}_3/\text{Mn}_3\text{O}_4$ and $\text{Co}_3\text{O}_4/\text{CoO}$ [44]. Fig. 6 shows equilibrium concentration as a function of temperature for these systems.

While fuel combustion decreases the oxygen concentration and improves the decomposition reaction of the metal oxide particles in the fuel-reactor, the metal oxide must be regenerated in the air-reactor, which constrains the temperature and oxygen concentration at the reactor outlet for thermodynamic reasons. To maintain high power plant efficiency, it is important to keep the outlet partial pressure of O_2 from the air-reactor as low as possible. Thus, the temperature in the air-reactor to oxidize the oxygen-carrier should be lower for Mn-based and Co-based oxygen-carriers than for Cu-based oxygen-carriers. In addition, for Cu-based and Mn-based oxygen-carriers, the reactions with carbon in the fuel-reactor are exothermic, allowing a lower temperature in the air-reactor than in the fuel-reactor facilitating their regeneration. This high temperature dependency

on oxygen concentration in the CLOU process makes thermal integration between fuel-reactor and air-reactor a key aspect in the development of this technology [47].

Fig. 6. Equilibrium partial pressure of gas-phase O_2 over different metal oxide systems.

Development of suitable materials for use as oxygen-carriers in CLOU is focused on copper oxide [46] or combined oxides of Mn with other metals, such as Ca, Mg, Cu, Fe and Si [48]. Combined oxides have not shown oxygen release capacities as high as that of copper oxide. When used in a continuous unit, they will act mainly as an oxygen-carrier for *i*G-CLC, but with the advantage of an additional contribution of gaseous oxygen. This new concept has been identified as Chemical-Looping aided by Oxygen Uncoupling (CLaOU) and is currently in its early stages of development [49].

4.3. Pilot testing for solid fuel CLC

Significant developments have been made in the combustion of solid fuels by CLC within the last decade [7]. CLC with solid fuels was first demonstrated at the 10 kW_{th} scale at CUT in 2008 [50]. Furthermore, results obtained with different oxygen-carriers, e.g. iron or manganese ores, and solid fuels, including coal and biomass, showed the reliability of this technology [6]. The state of the art is defined by the autothermic operation of a 1 MW_{th} unit at Darmstadt University of Technology (TUD) [51] and a 3 MW_{th} unit by Alstom USA [52]. However, optimal operation has

still not been achieved and feedback from small or pilot CLC units is required. The CLOU process was demonstrated at a lower scale (1.5 kW_{th}) at ICB-CSIC with a Cu-based oxygen-carrier [53], and further development of oxygen-carrier material is necessary before its scale-up.

A review showing the existing pilot units and one detailed analysis of continuous unit results found in the literature was produced by Adánez et al. [7]. In this work, relevant results were compared and evaluated, and three main parameters were defined for that purpose: (1) CO₂ capture efficiency (η_{cc}), which determines how much of the carbon converted in the CLC unit appears in any gaseous compound in the fuel-reactor; (2) combustion efficiency in the fuel-reactor ($\eta_{comb,FR}$), which is a measure of the gas conversion in the fuel-reactor, defined as the ratio of oxygen demanded by the unburnt products to the oxygen demanded by the solid fuel converted in the fuel-reactor; and (3) total oxygen demand (Ω_T), defined as the fraction of oxygen needed in the oxygen polishing related to the stoichiometric oxygen demanded for the combustion of the solid fuel.

CO₂ capture efficiency is dependent on parameters affecting char conversion reactions (gasification in *i*G-CLC or combustion in CLOU), such as char gasification/combustion rate, solids residence time in the fuel-reactor and carbon stripper separation efficiency. The oxygen transport capacity of the oxygen-carrier, R_{OC} , can affect CO₂ capture because the solids circulation rate required between fuel- and air-reactors depends on the R_{OC} value. The effect of oxygen-carrier reactivity is lower, as it is related to the decrease in the inhibitory effect of H₂ on the gasification reaction in *i*G-CLC. However, char gasification or combustion rates are highly dependent on temperature and solid fuel reactivity, which in the case of coals depends on rank.

To illustrate the above-mentioned effects, Fig. 7 provides some examples of the effect of operating variables on process performance. Fig. 7a shows the effect of temperature on CO₂ capture efficiency by *i*G-CLC with ilmenite and by CLOU with a Cu-based oxygen-carrier in a 1 kW_{th}

CLC unit without a carbon stripper. CO₂ capture efficiency is evidently much higher for CLOU than for *i*G-CLC because the combustion reaction rate is higher than the gasification rate.

Fig. 7. Effect of fuel-reactor temperature on (a) CO₂ capture and (b) combustion efficiency for *i*G-CLC or CLOU process, as well as (c) total oxygen demand for different fuels in *i*G-CLC [54].

Combustion efficiency in the fuel-reactor and total oxygen demand mainly depend on oxygen-carrier reactivity, solids circulation rate and oxygen-carrier inventory in the fuel-reactor. This is the main drawback of *i*G-CLC because Ω_T values are usually found in the 10–20 % range. Fig. 7b shows $\eta_{\text{comb,FR}}$ as a function of the temperature both for *i*G-CLC and CLOU. For CLOU, the combustion efficiency was always 100 % and total oxygen demand (Ω_T) was zero; but combustion efficiencies for *i*G-CLC increased with temperature, although only values in the 70–80 % range were found with ilmenite. Oxygen demand can be decreased by using more reactive oxygen-carriers, but complete combustion is achieved. In addition, total oxygen demand is highly affected by the type of fuel, as it is mainly dependent on the content and type of generated volatile matter; see Fig. 7c.

Some variable optimizations can be made to minimize oxygen demand. Thus, an increase in the solids inventory, and particularly in the oxygen-carrier-to-fuel ratio would decrease the oxygen demand [55]. In addition, some design modifications have been theoretically evaluated in order to minimize the presence of unburnt compounds and oxygen requirements [56], These measures

intend to achieve a better gas-oxygen-carrier contact or imply new design concepts for the current scheme of the *iG*-CLC system. Total oxygen demand as low as 0.9% has been estimated for an optimum case in which a carbon stripper is used as a secondary fuel-reactor. The implementation of these solutions in *iG*-CLC units is still ongoing.

The performance of CLC with solid fuels can be notably improved when oxygen-carriers with CLOU properties are used. However, few materials have been tested in a continuous CLC unit burning solid fuels, and further development of this type of materials is encouraged. With Cu-based or Cu-Mn mixed oxides, complete combustion was easily achieved with different fuels [57,58], but the materials must be improved before their scale-up in order to increase particle lifetime [32]. When oxygen transport capacity for CLOU was low, as in case of CaMn perovskite-type oxygen-carriers [59] or when MnFe mixed oxides [60] were used, significant improvements in the oxygen demand were found but a zero Ω_T value was not possible.

The fate of sulphur is a bit different depending on whether the conversion takes place in *iG*-CLC or CLOU mode. Common oxygen-carriers based on Fe, Cu and Mn oxides do not suffer from deactivation by S compounds. Most of the sulphur is in the fuel-reactor gas purifying CO₂ as SO₂ in CLOU, or SO₂-H₂S mixtures in *iG*-CLC, although the lower fuel flow and higher concentrations with respect to the air-reactor outlet allow easy separation.

4.4. Effects of solid fuel ashes

Although most of the ashes generated in a coal combustion plant is fly ash, which escape from the system, the fraction of bottom ashes remains in the CLC system and accumulates, reducing the oxygen-carrier inventory and leading to diminished performance of the system with regard to CO₂ capture and oxygen demand. Continuous draining of ashes must be performed in order to limit their concentration in the bed material, with an expected loss of oxygen-carrier material. Thus, an estimation of the lifetime of oxygen-carrier particles as a function of the bottom ash content in coal indicated important changes in their lifetime and makeup needs, and thus in costs. Separation

of the oxygen-carrier from ashes for reuse seems necessary in order to reduce makeup costs in the process, which are more significant for typically synthetic CLOU oxygen-carriers that are usually more expensive than the ores used in *i*G-CLC. In this sense, the magnetic properties of Mn-Fe materials can facilitate oxygen-carrier separation from ashes during solid fuel combustion [61]. Moreover, ashes can interact with the oxygen-carrier during solid fuel combustion, affecting its reactivity and oxygen transport capacity. The possible reactions taking place have been the subject of research in recent years [62]. The oxygen-carrier/ash interactions will vary with coal and biomass ash type, and other properties evidenced by the ash analysis, which must be evaluated. In the case of biomass ash, preliminary studies indicate the influence of the type of biomass used as fuel. The presence of silica in the ashes can lead to the formation of potassium silicates, facilitating the sintering of iron ore particles [63].

5. Process modelling and reactor design

Promising oxygen-carriers have been specifically developed for the combustion of every kind of fuel, and some of them have been used at the 0.1 MW_{th} scale for gaseous fuels, and 1 MW_{th} scale for solid fuels. The good results obtained during the experimental demonstration of CLC encourage its future scale-up, e.g. to 10 MW_{th} [64], with modelling tasks being a valuable tool in order to create a safe design for the CLC unit. Mechanistic models can predict the CLC performance by taking into account its individual parts. Results of mechanistic models would be subsequently included in process models to define the design and operating conditions that optimizes CLC performance.

5.1. Mechanistic models

Relevant progress has been achieved in the modelling of the reactors comprising a CLC unit, mainly considering the use of two interconnected fluidized-bed reactors. Theoretical models must

properly describe the fluid-dynamics of the reactors, the kinetics of the reactions involved in each CLC unit, and the heat transfer processes associated with the chemical reactions.

The mixing and contact between gas and solids in a fluidized bed is described by fluid dynamics, which must take into account the distribution of solids in the reactor and the restrictions hindering the gas from reacting with the solids, e.g. diffusional resistance from the bubbles to the emulsion phases. Fluid dynamics models can be differentiated into two categories, macroscopic models and computational fluid dynamic (CFD) models.

CFD models make use of complex calculus to consider the geometry and physical processes, which requires a large computation effort. But this effort is rewarded by a detailed description of the flows inside the CLC unit [65]. Due to their inherent complexity, most CFD models have been simplified to consider uniquely either the dense bed in the bubbling regime, or the dilute region in the turbulent or high-velocity regime.

The method used by macroscopic models is simpler, involving empirical equations to describe the characteristic flows of particles and gas in the fluidized bed. Despite their simplicity, these models are able to properly describe the distribution of gas and solids along the reactor considering the two-phase theory for bubbling or circulating fluidized beds [66]. Macroscopic models have been used to simulate the performance of CLC pilot plants up to the scale of 1 MW_{th} even in cases where the reactor was a CFB, and with the advantage of having short computing times [67].

The model must also include a reasonable description of the chemical processes involved in the fuel conversion and the oxygen transfer in relation to the oxygen-carrier. Simplified reaction mechanisms, considering simple and discrete reactions, are mostly used. The oxidation of CH₄ by the oxygen-carrier is often considered to occur in two steps, with carbon, CO and/or H₂ appearing as intermediate products of the reaction. Additional reactions can also be relevant in the fuel-reactor, e.g. methane cracking and reforming, or water gas shift, which are more relevant for Ni-based oxygen-carriers [68]. Reactions when several reducing agents are present in the gas mixture

must be carefully evaluated [69]. When a solid fuel is used in the *i*G-CLC process, the devolatilization of the fuel particles and the gasification of char are reactions that must be considered in the reaction scheme [67]. Additionally, the oxygen uncoupling reaction (R8) and fuel combustion with released oxygen is included in the CLOU models [70].

At this stage, the fuel conversion rate will be determined by the kinetics of every reaction considered in the reaction scheme. The interaction between the active phase and the supporting material in the oxygen-carrier affects reactivity, and it is necessary to determine the kinetics parameters for each specific oxygen-carrier. The determination of the activation energy and the reaction order of each reaction must be evaluated for relevant CLC conditions, i.e. a broad range of reacting gas concentrations and a temperature interval of 800-1000 °C are usually considered. In addition, the kinetics at pressurized conditions have to be determined in order to model CLC units at pressures above atmospheric pressure. Pressure increase has a beneficial effect on the reaction rate, but lower than expected [71].

The rate-controlling mechanism can change in the course of the reaction. Often, a nucleation step can be relevant during the initial induction period at low reacting temperatures. However, the main reaction is usually controlled by the chemical reaction on the surface of the pores or grains inside the particle. Eventually, the reaction rate can slow down during the last stage due to the relevance of solids diffusion in the product layer. Considering the characteristics of particles used as oxygen-carriers, homogeneous conversion and temperature can be assumed in the whole particle in most of cases [72]. Models based on nucleation and nuclei growth or the Changing Grain Size Model (CGSM) are often used for kinetics determination. In addition, the kinetics of individual particles must be applied, taking into consideration the residence time distribution of oxygen-carrier particles inside the reactor [20].

Fluid dynamics and chemical reactions must be linked to the heat transfer processes. An isothermal reactor is usually considered for lab-scale CLC units. Nevertheless, heat transfer should

be included in the scale-up of CLC technology in order to examine possible problems related to the non-isothermicity of the reactor [73]. In addition, the design of the cooling surfaces will be a key issue in the scale-up of the CLC process in order to maintain the heat balance in the system [74].

To guarantee confidence in the modelling results, the reactor model must be previously validated against experimental results. For example, macroscopic models have been validated against experimental results obtained at a higher scale of CLC technology, i.e. up to 0.1 MW_{th} for gaseous fuels [75] and up to 1 MW_{th} for solid fuels [76,77].

Validated models have been used to simulate the effect of operating conditions on fuel conversion and determine optimal conditions for the design of a CLC unit. For example, operation in the turbulent regime is recommended in order to achieve full conversion of gaseous fuels [78], but the bubbling regime could also be feasible for solid fuels [79]. Theoretical calculations suggest that a solids inventory in the fuel-reactor in the 150-250 kg/MW_{th} interval is feasible to fully convert gaseous fuels, whereas increasing these values to above 500-750 kg/MW_{th} is not recommended for solid fuels in *iG*-CLC, even if the complete combustion is not still achieved. However, lower solids inventories, in the order of 150 kg/MW_{th}, could be valid for solid fuels in CLOU [80].

Considering the optimum conditions from modelling results, some attempts have been made to create a preliminary design of the basic parameters for the scale-up of a CLC unit. Thus, for natural gas combustion, the cross-section area of the fuel- and air-reactors has been calculated to be 0.1 and 0.2 m²/MW_{th} in order to maintain a gas velocity of about 1 and 6 m/s, respectively, and the pressure drop in the 10-20 kPa interval [81]. In order to limit the pressure drop in the fuel-reactor in *iG*-CLC with solid fuels, the cross-section area of the fuel-reactor should be slightly higher (~0.25 m²/MW_{th}) compared to the use of gaseous fuels [74].

The use of validated theoretical models for design purposes must be promoted in the future. Given their simplicity, macroscopic models have a great potential for the optimization of both design

parameters and operating conditions. A detailed design of a CLC unit for engineering purposes can be furthered using CFD models that take into account the relevant results achieved by macroscopic models.

5.2. Process models

Modelling results and design conditions, such as combustion efficiency, reactor temperatures and heat management of the CLC unit, will affect the energetic efficiency of the process. Optimum conditions would depend on the final use of the energy obtained from the combustion process in a CLC unit. The combustion of gaseous fuels at atmospheric pressure and relatively low temperature (700-900 °C) could be sufficient for industrial processes where heat is required, such as refineries. Higher temperatures (~1000 °C) would be required for *iG*-CLC in order to improve the coal conversion.

However, pressurized conditions at a higher temperature (1200 °C) would be necessary to provide high energy efficiency (54%) for electricity generation taking advantage of a combined cycle. However, energy efficiency falls to 44% when the CLC unit is operated at 900°C, which is similar to the efficiency of a CLC unit at atmospheric pressure [17].

Values of 41-42 % are calculated for the energetic efficiency of the *iG*-CLC process with coal [82], but higher efficiencies (46-48 %) are predicted for the CLOU process due to the inherent improvement in combustion efficiency and the avoidance of using steam as the gasifying agent in the fuel-reactor [83].

Therefore, modelling work is a relevant tool in order to determine the design and operating conditions affecting the combustion efficiency of the fuel, first, and the energy efficiency of the whole CLC unit, second. In this sense, special attention should be paid to parameters such as reactor temperature, pressure drop, steam requirements (specifically for *iG*-CLC) and air excess ratio [7].

6. Final considerations and research needs.

The suitability of the CLC process with gaseous fuels has been demonstrated in units with very different design concepts and mainly at small scale (10-120 kW_{th}). Therefore, the next step in the development of CLC technology is the scaling-up of the process to demonstration scale. Scaling up to 10 MW for demonstration during long periods needs to be addressed in order to reach the next level of maturity for the scale-up step before pre-commercial units.

The core of the performance of CLC with gaseous fuels is based on the oxygen-carrier used, which has consequences on the design of the unit, environmental issues and the cost of CO₂ capture. Research into oxygen-carriers has focused on the development of reactive, environmentally friendly and sulphur-resistant materials. There is presently a portfolio of oxygen-carriers suitable for the process, and important efforts are being invested into the scale-up of oxygen-carrier production to industrial scale. Increasing the lifetime of the oxygen-carrier requires reducing attrition rates during the process. There is a great deal of uncertainty. Oxygen-carrier attrition can be affected by several factors. One of these is the physical attrition resulting from abrasion and erosion to the particles inside the fluidized beds. This can be reasonably predicted by such standard tests as ASTM-5858. However, chemical stresses resulting from continuous changes to structure and volume have one important effect and explain the differences found between particles not reacted after use. Cabello et al [84] proposed one methodology that applies the jet attrition test (ASTM-D-5757) to particles reacted different times in a continuous CLC unit. There have recently been clear indications [32, 85] that chemical stress is related to the change in conversion of the oxygen-carrier during redox process. The intensity of these effects is also material dependent. This is a fundamental field of research in order to reduce the CO₂ capture costs, as attrition is the main added cost for CO₂ capture by CLC.

The development of the CLC process under pressure, in order to take advantage of pressure on process efficiency, is an important challenge for the deployment of this technology for gaseous fuels.

Solid fuels CLC has been demonstrated at different scales from bench to pilot and semi-industrial level with coals and biomass using *i*G-CLC and CLOU processes. Combustion has been performed using mainly ores and wastes as oxygen-carriers, although synthetic oxygen-carriers have also been used, especially for CLOU. The results obtained show the suitability of the process, although they also indicate that the process needs additional advances in order to improve CO₂ capture and oxygen demand if complete combustion of gases at the fuel-reactor outlet is to be achieved.

Extrapolation of the results obtained in the autothermal pilots used to demonstrate the process is difficult, owing to the difficulties in independently modifying operating variables. One possible solution could be the use of models, containing independently evaluated kinetic and flow parameters. These models need to be validated under highly-controlled conditions, in units of the same kind of flow, at different combinations of operating conditions. This is expected to allow safe extrapolation could be made.

CO₂ capture can be improved, both for *i*G-CLC and for CLOU, using an efficient carbon stripper. Process intensification combining a carbon stripper and fuel-reactor in the same reactor unit reduces process complexity and minimizes overall steam needs.

Some process modifications have been proposed in order to minimize or to eliminate the oxygen polishing step needed to solve the oxygen demand of gases coming from the fuel-reactor, although they have not yet been tested. Another solution is the use of oxygen-carriers with pure CLOU properties or mixed CLC + CLOU properties. Consequently, if the CLOU mechanism is high enough, the combustion of fuel-reactor outlet gases will be complete and the oxygen polishing

step avoided. There is still a need at present for resistant oxygen-carriers that can be easily separable from ashes for their reuse.

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