

# Developments in Chemical Looping Technology Worldwide



Tiruchirappalli Regional Engineering College  
Science and Technology Entrepreneurs Park

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EUROPEAN UNION



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## Executive Summary

This report focuses on the comprehensive review of the main developments in the “Chemical-Looping Technology” worldwide. This technology is based on the transfer of the oxygen from air to the fuel by means of a solid oxygen carrier avoiding direct contact between fuel and air for different final purposes.

There is a growing concern that anthropogenic carbon dioxide ( $\text{CO}_2$ ) emissions are contributing to global climate change. Therefore, it is critical to develop technologies to mitigate this problem. Chemical Looping Combustion (CLC) is a promising technology for fossil fuel combustion preventing  $\text{CO}_2$  dilution with flue gases, mainly nitrogen. In CLC, the oxygen required for the combustion of fuel is being supplied by the solid oxygen carrier and hence the combustion products ( $\text{CO}_2$  and water) are free of nitrogen, which facilitate easier separation of  $\text{CO}_2$  from water. As a result, the requirement of  $\text{CO}_2$  separation from flue gases, a major cost for  $\text{CO}_2$  capture, is circumvented. Furthermore, formation of  $\text{NO}_x$  is also reduced. Hence CLC has emerged during last years as a very promising technology for power plants and industrial applications with inherent  $\text{CO}_2$  capture mechanism, which avoids the energy penalty when compared with other competing technologies.

This report discusses the need for the carbon dioxide capture and storage (CCS) and briefly reviews the technologies available for  $\text{CO}_2$  capture. The CLC process is described in detail in the report and the progress made in the last few years in the development of CLC regarding the use of gaseous and solid fuels, the oxygen carrier materials, the continuous operation experiences worldwide, different variations in CLC designs and the modelling works carried out are discussed in detail in the report. Finally the future research needs and key conclusions are marked in the last section of the report.

This report discusses the potential of CLC technology in power plants, especially for the countries with large coal reserves such as India, where the major thermal power production is from coal. This technology can be considered as a good option for the power plants to reduce their carbon foot print. This report can be used as a ready reference for disseminating the knowledge about the Chemical Looping Combustion technology for the power plant engineers of our country.

## 1. Introduction

### 1.1 Concerns about Global Warming

Global warming is the increase in the average temperature of Earth's near-surface air and oceans. The increase in concentration of some greenhouse gases (GHGs) in the atmosphere is expected to cause global warming and thus create changes in the world's climate. As shown in Figure 1.1, the short wave radiation from the sun penetrates the atmosphere and reaches the earth's surface. As the earth's surface is heated up, long wave radiation is emitted which is subsequently absorbed by greenhouse gases such as water vapour, carbon dioxide, methane, nitrous oxide, and aerosols, thus trapping heat. At general thermal equilibrium conditions, this keeps the earth's surface warm at an average temperature of 17°C. However, excessive emission of the above-mentioned gases could trap more heat, thus increasing the average temperature.

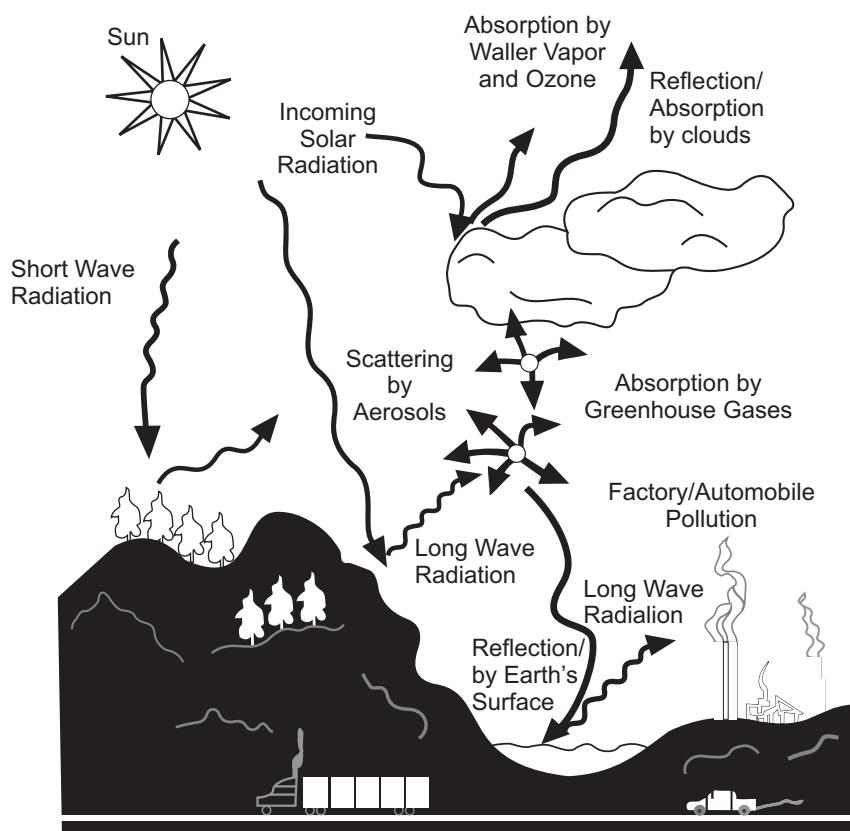


Figure 1.1 Entrapment of part of the heat radiated from the earth's surface by GHGs

According to Intergovernmental Panel on Climate Change (IPCC) report, eleven of the recent years (1995-2006) rank among the twelve warmest years in the instrumental record of global surface temperature since 1850. Most of the Climate model projections summarized in the latest IPCC report indicate that the global surface temperature is likely to rise a further 1.1 to 6.4 °C (2.0 to 11.5 °F) during the 21st century. Climate change can strongly modify the biodiversity on the earth. Global

warming has a severe effect on the life systems present in earth. One example of the ill-effect of global warming is the melting of polar ice caps. This leads to increase in the sea level which further leads to submerging of huge areas of land. The melting of polar ice caps has also propelled the devastation of polar bears. Other likely effects of global warming include changes in the frequency and intensity of extreme weather events, species extinctions, and changes in agricultural yields. Warming and related changes will vary from region to region around the globe, though the nature of these regional variations is uncertain.

Among the possible causes, it seems that observed temperature increase since the middle of the 20th century was very likely caused by increasing concentrations of greenhouse gases resulting from human activity such as fossil fuel burning and deforestation. There are several greenhouse gases emitting from human activities, each of one presenting different global warming potential (GWP) [1]. The concept of GWP takes account of the gradual decrease in concentration of a trace gas with time, its greenhouse effect whilst in the atmosphere and the time period over which climatic changes are of concern. The main gases affecting the greenhouse effect are H<sub>2</sub>O, CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, CFC's and SF<sub>6</sub> [2]. The contribution to the global greenhouse effect of the different gases is related to their GWP and to the concentration in the atmosphere at a given time. In this sense, CO<sub>2</sub> is considered as the gas making the largest contribution to the GHG effect as a consequence of two factors. The first one is that CO<sub>2</sub> represents the largest emissions of all the global anthropogenic GHG emissions, with percentage values as high as 75%. The second one is their high residence time in the atmosphere: the lifetime of CO<sub>2</sub> from fossil fuel uses might be 300 years, plus 25% that lasts forever [3].

## 1.2 Need for CO<sub>2</sub> Capture and Storage (CCS) Technologies

The carbon dioxide concentration in the atmosphere has increased strongly over the few past decades as a result of the dependency on fossil fuels for energy production. Looking at the energy production scenario in India, as per the data from Ministry of Power, Government of India (as shown in Figure 1.2), the power production from installed plants in India - is primarily from thermal sources compared to renewable, hydro and nuclear sources. In turn, coal is the major thermal source for power production in India. According to Integrated Energy Policy (IEP) committee, Coal will remain as a primary energy source till 2031-32. Hence, the CO<sub>2</sub> liberation from the power production is inevitable.

The global atmospheric concentration of CO<sub>2</sub> increased from a pre-industrial value of about 280 ppm to 390 ppm in 2010 [4]. Correlations have been found between the global average

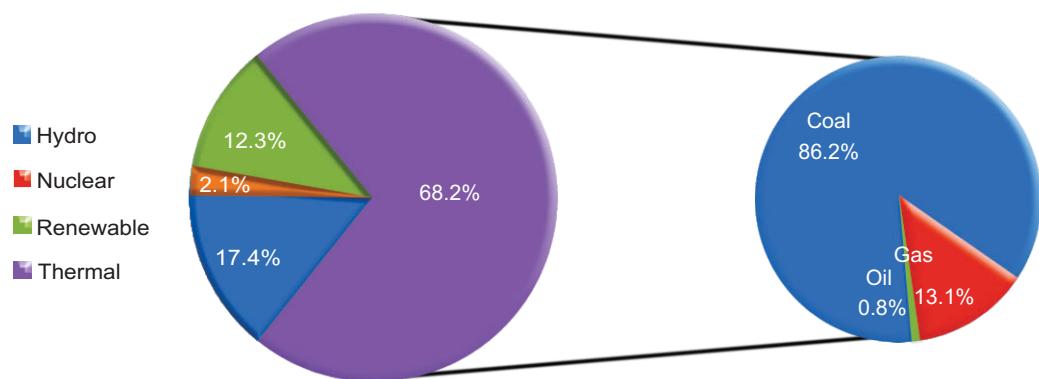


Figure 1.2. Sources for power generation in India

temperature and CO<sub>2</sub> concentrations in the atmosphere. The IPCC has suggested a 50–85% reduction in total CO<sub>2</sub> emission by 2050 to limit the anticipated global temperature rise to 2°C. To assure the increase in average temperature to be lower than 2 °C, which is considered as the limit to prevent the most catastrophic changes in earth, the CO<sub>2</sub> concentrations must not exceed 450 ppm. This means that the CO<sub>2</sub> atmospheric concentration must raise no more than 15% over today's concentration. Therefore, it is generally accepted that a reduction in emissions of greenhouse gases is necessary as soon as possible. In 1997, the nations participating in the United Nations Framework Convention on Climate Change (UNFCCC) drafted the historic agreement known as the Kyoto Protocol [5]. After ratification in 2005, its provisions include a mean reduction in the GHG emissions of the 39 developed countries of 5.2% over the period 2008 - 2012 compared to 1990 levels. Up to now, the technological options for reducing net CO<sub>2</sub> emissions to the atmosphere have been focused on [6]:

- (i) reducing energy consumption, by increasing the efficiency of energy conversion and/or utilization
- (ii) switching to less carbon intensive fuels
- (iii) increasing the use of renewable energy sources (bio fuel, wind power, etc.) or nuclear energy and
- (iv) sequestering CO<sub>2</sub> by enhancing biological absorption capacity in forest and soils.

It is clear that no single technology option will provide all of the emissions reductions needed. Even, the added efforts of all the above solutions will probably not allow reaching the desired low levels of CO<sub>2</sub> emissions. Under this context, CO<sub>2</sub> Capture and Storage (CCS) appears as an additional option necessary to reach the above objectives. It must be considered that energies from fossil sources (gas, oil and coal), those giving off CO<sub>2</sub>, will still satisfy over 80% of the energy demand during the first part of the 21st century, and unfortunately they will not yet be ready to be substituted by renewable sources massively in the near future [7]. According to the analysis made by the IPCC and

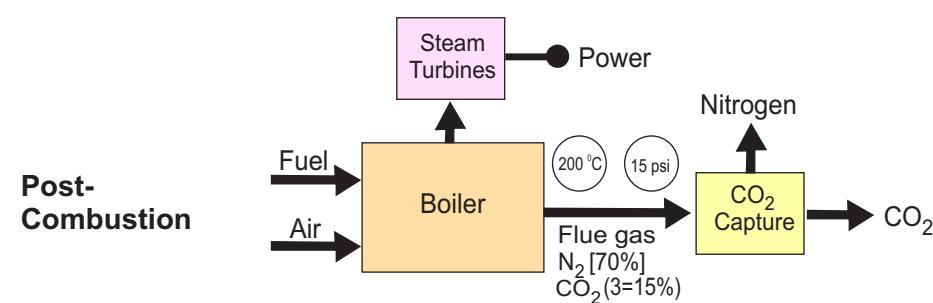
IEA [6,8], the CCS could account for 19% of the total CO<sub>2</sub> emission reductions needed in this century to stabilize climate change at a reasonable cost. Therefore, the development of CCS technologies to market maturity is essential for the production of clean energy from fossil fuels both to ensure a continued role of these fuels, in particular coal, as well as to reduce CO<sub>2</sub> global emissions [9].

### 1.3 What is CCS?

By definition, CCS is the capture, transportation and storage of CO<sub>2</sub> in underground storage locations. The purpose of CCS technology is to produce a concentrated stream of CO<sub>2</sub> from industrial and energy-related sources, transport it to a suitable storage location, and then store it away from the atmosphere for a long period of time. The IPCC Special Report on Carbon Dioxide Capture and Storage [6] gives an overview of the different options available for the capture, transport and storage processes.

### 1.4 CO<sub>2</sub> capture processes – Post, Oxy and Pre – Combustion systems

In consideration of how best to improve CO<sub>2</sub> capture, there are three most investigated technological pathways that can be pursued for CO<sub>2</sub> capture from industrial and power plants: post-combustion capture, pre-combustion capture, and oxy-combustion, as illustrated in Figure 1.3. In post-combustion capture, the CO<sub>2</sub> is separated from other flue gas constituents either originally present in the air or produced in combustion by e.g. chemical absorption using amines. In pre-combustion capture, the CO in the synthetic gas produced from gasification is transformed to H<sub>2</sub> and CO<sub>2</sub> via the water gas shift reaction, giving a gas with mainly H<sub>2</sub> and CO<sub>2</sub> and the CO<sub>2</sub> is then separated from the H<sub>2</sub> prior to combustion. In oxy-combustion, the fuel is burned in an oxygen stream that contains little or no nitrogen. All these technologies have undergone a great development during the last years and some of them are available at commercial scale.



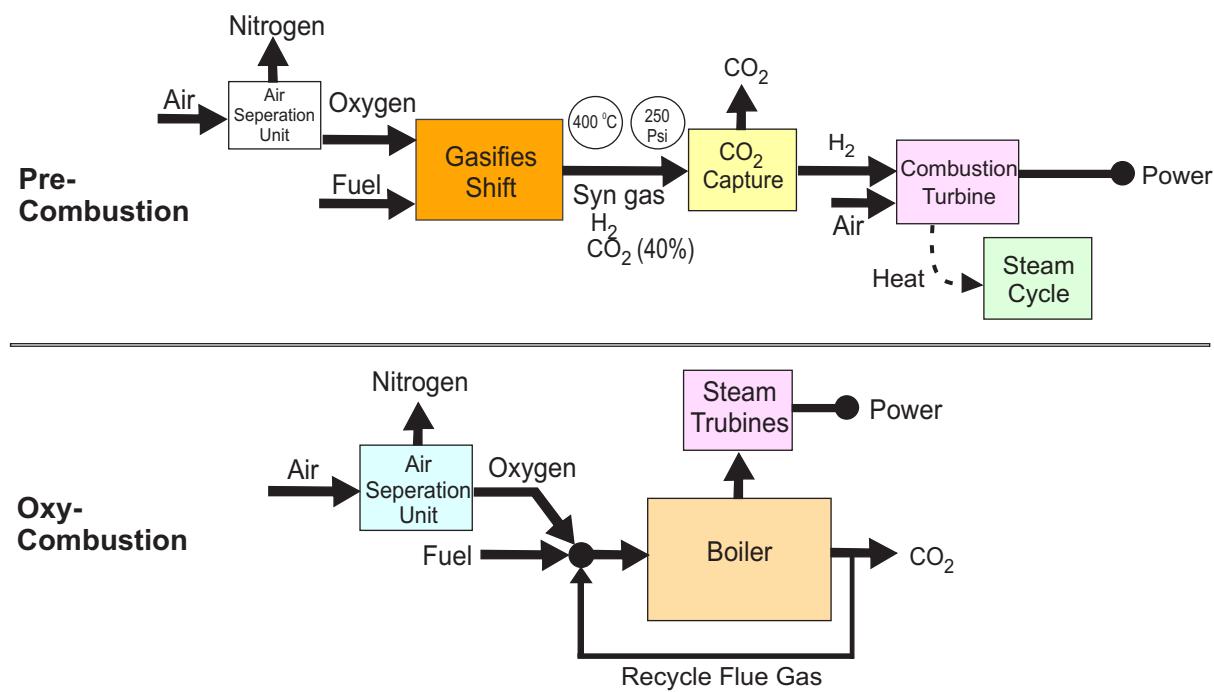
Figure 1.3 CO<sub>2</sub> capture technologies

Table 1 [10] provides a summary of the inherent advantages and disadvantages of each of these pathways. Post-combustion capture applies primarily to coal-fuelled power generators that are air fired. Pre-combustion capture applies to gasification plants. Oxy-combustion can be applied to new plants or retrofitted to existing plants.

Table 1 - Advantages and disadvantages of different CO<sub>2</sub> capture approaches

|                 | Advantages   | Barriers to implementation  |
|-----------------|--|---|
| Post-combustion | <ul style="list-style-type: none"> <li>Applicable to the majority of existing coal-fired power plants</li> <li>Retrofit technology option</li> </ul>   | Flue gas is ... <ul style="list-style-type: none"> <li>Dilute in CO<sub>2</sub></li> <li>At ambient pressure</li> </ul> ... resulting in ... <ul style="list-style-type: none"> <li>Low CO<sub>2</sub> partial pressure               <ul style="list-style-type: none"> <li>Significantly higher performance or circulation volume required for high capture levels</li> <li>CO<sub>2</sub> produced at low pressure compared to sequestration requirements</li> </ul> </li> </ul> |
| Pre-combustion  | Synthesis gas is ... <ul style="list-style-type: none"> <li>Concentrated in CO<sub>2</sub></li> <li>High pressure</li> </ul> ... resulting in ... <ul style="list-style-type: none"> <li>High CO<sub>2</sub> partial pressure               <ul style="list-style-type: none"> <li>Increased driving force for separation</li> <li>More technologies available for separation</li> <li>Potential for reduction in compression costs/loads</li> </ul> </li> </ul> | <ul style="list-style-type: none"> <li>Applicable mainly to new plants, as few gasification plants are currently in operation</li> <li>Barriers to commercial application of gasification are common to pre-combustion capture</li> </ul> <ul style="list-style-type: none"> <li>Availability</li> <li>Cost of equipment</li> <li>Extensive supporting systems requirements</li> </ul>  |
| Oxy-combustion  | <ul style="list-style-type: none"> <li>Very high CO<sub>2</sub> concentration in flue gas</li> <li>Retrofit and repowering technology option</li> </ul>  | <ul style="list-style-type: none"> <li>Large cryogenic O<sub>2</sub> production requirement may be cost prohibitive</li> <li>Cooled CO<sub>2</sub> recycle required to maintain temperatures within limits of combustor materials               <ul style="list-style-type: none"> <li>Decreased process efficiency</li> <li>Added auxiliary load</li> </ul> </li> </ul>  |

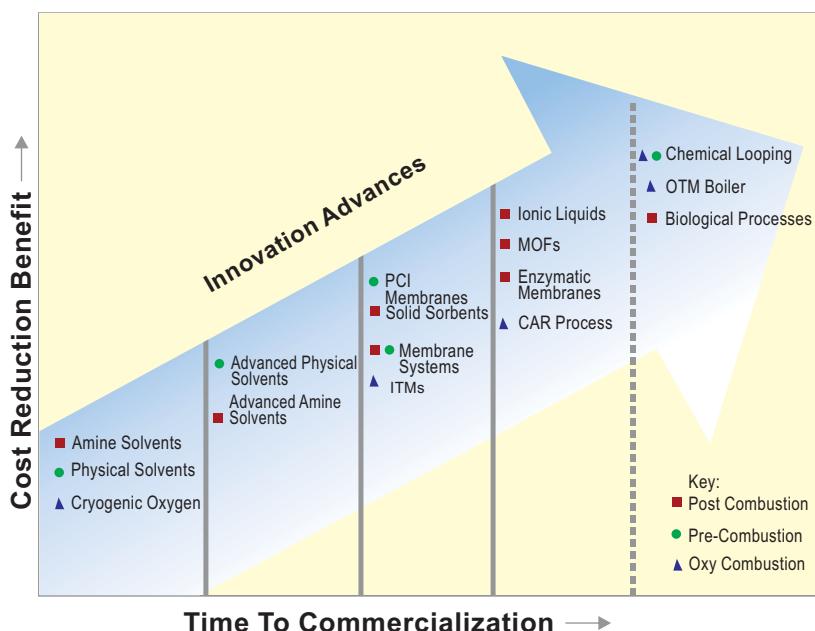


Figure 1.4 Innovative CO<sub>2</sub> capture technologies - cost reduction benefits versus time to commercialization

Figure 1.4 indicates that as innovative CO<sub>2</sub> capture and separation technologies advance significant cost reduction benefits can potentially be realized once they are commercialized. Technologies shown include both those funded by the DOE as well as those that do not receive funding from the DOE's Carbon Sequestration Program.

### 1.5 Chemical Looping Combustion (CLC) – Promising Capture option

Although the CO<sub>2</sub> capture technologies can reduce CO<sub>2</sub> emissions, they also have a high energy penalty, which results in a reduction of energy efficiency of the processes and thus increases the electricity or final energy cost. It is therefore favoured to investigate and develop other inexpensive CO<sub>2</sub> capture technologies. Significant work has undergone across the world during last few years to develop new low-cost CCS technologies. The objective was to identify the most promising technologies that had the potential to deliver performance and efficiency improvements resulting in close to a 50% reduction in the cost of CO<sub>2</sub> capture. Among them, the Chemical-Looping Combustion (CLC) process was suggested among the best alternatives to reduce the economic cost of CO<sub>2</sub> capture [11]. Moreover, the IPCC in their special report on Carbon Dioxide Capture and Storage identified CLC as one of the cheapest technologies for CO<sub>2</sub> capture. Later, the EU project “Enhanced Capture of CO<sub>2</sub>” (ENCAP) focused the research on the development of cost efficient pre-combustion and oxy-fuel processes for CO<sub>2</sub> capture, including CLC [12]. Taken as a reference for a pulverised fuel fired power plant without CO<sub>2</sub> capture using bituminous coal as fuel, the increase in

the electricity generation cost for a CLC plant was about 12 - 22%. The incremental in the electricity cost was lower when compared with for other technologies of CO<sub>2</sub> capture. The estimated cost of the capture per tonne of CO<sub>2</sub> avoided was 6 - 13 € for CLC. Similar evaluations concluded that the cost was 18 - 37 € for a pre-combustion technology using IGCC, and 13 - 30 € for an oxy-fuel process. Additionally, if the environmental impact is also considered, CLC is even more preferred to other CO<sub>2</sub> capture options.

The main weakness attributed to CLC was a very low confidence level as a consequence of the lack of maturity of the technology. It must be considered that this is an emerging technology. However, during the last 10 years it has experienced a great development as shown in the recent review article [13].

## 1.6 What is CLC?

Different Chemical-Looping cycles have been proposed for CO<sub>2</sub> capture including both the transference of CO<sub>2</sub> or oxygen [14]. Commonly, the term Chemical-Looping is referred to those processes transporting oxygen. Thus, the term “Chemical-Looping” has been used for cycling processes that use a solid material as oxygen-carrier containing the oxygen required for the conversion of the fuel. To close the loop, the oxygen depleted solid material must be re-oxidized before starting a new cycle. The final purpose of the conversion of the fuel can be the combustion or the hydrogen production. Table 2 shows a summary of different Chemical-Looping processes proposed in the literature.

For combustion purposes, the oxygen depleted solid material must be regenerated by oxygen in air. In general, these processes are known with the general term “Chemical-Looping Combustion” (CLC). CLC processes can address gaseous or solid materials as primary fuels. In CLC of gaseous fuels, the oxygen carrier reacts directly with the fuel e.g. natural gas, refinery gas, etc. Different possibilities arise for processing solid fuels as coal, biomass, etc. In the Syngas-CLC process, the oxygen-carrier comes into contact with the gasification products (syngas) obtained in a gasifier. In this process, the fuel fed into the CLC system is gaseous although the primary fuel is solid. To avoid the gasifier, solid fuel and oxygen carrier can be mixed in a unique reactor. In the in-situ Gasification CLC (iG-CLC) process, the oxygen carrier reacts with the gasification products of the solid fuel generated inside the fuel reactor. Additionally, in the process called Chemical-Looping with Oxygen Uncoupling (CLOU), the oxygen-carrier is able to release gaseous oxygen for the combustion of the solid fuel.

For hydrogen production, the regeneration of the oxygen-carrier can be done using air or steam. When air is used for regeneration, it can be differentiated: the Steam Reforming integrated to Chemical-Looping Combustion process (SR-CLC), where CLC is used to give the energy required for usual catalytic steam reforming; and the Chemical-Looping Reforming process (CLR) where primary products from the Chemical-Looping system are H<sub>2</sub> and CO. Other processes use the property of some oxygen depleted materials to react with steam to produce hydrogen, also known as “water splitting”. In this category it can be found the Chemical-Looping Hydrogen (CLH) or “One Step Decarbonization” (OSD) process, and the so-called “Chemical-Looping Gasification” technologies: the Syngas Chemical-Looping process (SCL) and the Coal Direct Chemical-Looping process (CDCL). Usually these processes need several oxidation steps using air for the final regeneration of the oxygen carrier.

Table-2: Summary of the Chemical Looping processes for CO<sub>2</sub> capture.

| Aim                       | Primary Fuel | Process    | Main features  |
|---------------------------|--------------|------------|--|
| Combustion                | Gas          | CLC        | Gaseous fuels combustion with oxygen carriers  |
|                           | Solid        | Syngas-CLC | Previous gasification of solid fuel Oxygen requirement for gasification  |
|                           | Solid        | iG-CLC     | Gasification of the solid fuel inside the fuel reactor<br>Low cost oxygen carriers are desirable   |
|                           | Solid        | CLOU       | Use of oxygen carriers with gaseous O <sub>2</sub> release properties<br>Rapid conversion of the solid fuel  |
| H <sub>2</sub> production | Gas          | SR-CLC     | Steam reforming in usual tubular reactors  |
|                           | Gas          | a-CLC      | Partial oxidation of fuel with oxygen carriers instead gaseous O <sub>2</sub><br>Process can be fit to produce pure N <sub>2</sub> stream and the desired CO/H <sub>2</sub> ratio                  |
|                           | Gas          | CLH(OSD)   | H <sub>2</sub> is produced by oxidation with steam of the oxygen carrier<br>Three reactors are needed (FR, AR, Steam reactor)  |
|                           | Solid        | SCL        | H <sub>2</sub> is produced by oxidation with steam of the oxygen carrier<br>Previous gasification of solid fuel with O <sub>2</sub><br>Three reactors are needed (reducer, oxidizer and combustor) |
|                           | Solid        | CDCL       | H <sub>2</sub> is produced by oxidation with stream of the oxygen carrier<br>Coal & O <sub>2</sub> are fed to the reducer reactor<br>Three reactors are needed (reducer, oxidizer and combustor)   |

This report focuses on the overview of the history of the above referred Chemical -Looping Combustion giving the main milestones reached during last years in the development of the technology, which will be useful for all the power plant practitioners.

The basic idea can be first attributed to Lewis and Gilliland [15] who indicated, that the development of CO<sub>2</sub> capture technologies in a global context of power generation processes should include also solid fuels as energy sources. In this context, CLC can directly use solids fuels without the need of a previous gasification. Lyon and Cole [16] proposed in 2000 unmixed combustion for solid fuels. The first experiments in a CLC system with solids fuels were accomplished by Lyngfelt's research group at CHALMERS in 2005 as part of the EU project "Enhanced Capture of CO<sub>2</sub>"(ENCAP) [17,18]. They tested the combustion of a bituminous coal and petcoke in a 10 kWth experimental rig for solid fuels. The major changes to adapt CLC to solid fuels are related with the fuel-reactor design and the type of oxygen-carrier. In this case, ilmenite was selected as the oxygen carrier.

Moreover, a first concept design of a 455 MWe CLC solid fuel power plant was also accomplished within the project. The development of the CLC technology for use of solids fuels continued within the EU project "Emission Free Chemical Looping Coal Combustion Process" (ECLAIR), which started in 2008. The key issues considered in the project are related to i) verification of oxygen-carrier performance, ii) demonstration of the technology in a 1MWth CLC system and iii) finding adequate technical solutions to the reactors and surrounding systems [19]. Within this project, another technology valid for solid fuels is also under development: the Chemical-Looping with Oxygen Uncoupling (CLOU) process. This new process was proposed by Mattisson et al. [20] based on the CuO decomposition properties already noted by Lewis and Gilliland [21]. The chemical looping processes have been also developed in USA. The research group of Prof. Fan at the Ohio State University (OSU) has been involved in several American projects with the main objective to develop the coal direct chemical looping (CDCL) process [22,23] by using iron oxide as oxygen carrier. The fuel reactor consists of a moving-bed and the air reactor is an entrained flow reactor. This technology can be used to produce electric power or H<sub>2</sub> if the oxidation is carried out by air or steam, respectively.

ALSTOM worked in a multi-phase program to develop the "Hybrid Combustion-Gasification Chemical Looping Process" where CaSO<sub>4</sub> is used as oxygen-carrier for heat generation, syngas production or hydrogen generation [24, 25]. Substantial work began in 2003 with the construction of a small-scale pilot facility of 65 kWth (Process Development Unit, PDU) in Windsor, Connecticut. Later phases include the design, construction and operation of a 3-MW<sub>th</sub> prototype facility that it was expected to be operational in 2012.

The interest in CLC technologies is continuously increasing because of the promising results showed above. Chemical-Looping processes had about 3500 hours of operational experience in continuous plants of different size, with 36 different materials tested. Considering that the experimental experience of this technology is less than 10 years old, the development of the process can be considered very successful. This is also supported by the increasing number of papers, patents [21,26-28], and PhD Thesis [29,30] in subjects related with CLC and CLR. Patents cover different aspects of the technology development including oxygen carrier manufacture, reactor configuration, plant optimization and even new processes related to CLC. A quick overview of the status of the development of the Chemical-Looping processes was done by Lyngfelt et al. in 2008 [31]. In the same year, Hossain and de Lasa [32] reviewed the progress reached in the development of oxygen carrier materials. Later, the applications of Chemical-Looping technologies for fossil energy conversion were briefly overviewed by Fan and Li [33], and Fang et al[34]. A deeper description of Chemical-Looping technologies has been done recently by Fan [22] and by Brandvoll [35]. Finally, Lyngfelt [36] have Combustion process using gaseous and solid fuels, respectively.

### **1.7 Energy efficiency comparison of different plants with CLC**

Existing dependence on the coal based power plants to meet the increasing electricity demand cannot be changed abruptly. Hence developing efficient coal based power plants with low emissions is of great demand. IGCC plants are established technologies for this purpose. However, CO<sub>2</sub> capture still causes substantial reduction in efficiency due to the energy demand for CO<sub>2</sub> separation and compression for transport and storage of it. This section will give a brief comparison of the efficiency of the conventional power plants and IGCC with CO<sub>2</sub> capture system and the plants with CLC technology, based on different studies reported in the literature. The coal based conventional IGCC technology without carbon capture has a net electrical efficiency in the range of 42–46% and specific carbon dioxide emission in the range of 700–800 kg/MWh<sub>e</sub> [37-40]. But an efficiency drop of 10-12% is estimated due to the CO<sub>2</sub> capture unit addition [41]. Therefore simulation studies have been carried out showing the feasibility of integrating chemical looping combustion (CLC) consumes less energy for CO<sub>2</sub> capture unit.

Enlarch et al. analysed the performance of various configurations of CLC used in integrated gasification combined cycle power plants (CLC-IGCC) and compared to a conventional IGCC design with pre-combustion carbon capture by physical absorption [42]. He reported an overall efficiency of 37.7% for CLC-IGCC where as 34.9% for conventional IGCC. An exergy analysis was performed to identify the sources of thermodynamic inefficiencies. This revealed that within the components required for the carbon capture in the IGCC design, namely the water gas shift reactors and acid gas removal with CO<sub>2</sub> absorption, energy is destroyed at a rate of 157 MW, or 6.8% of the overall fuel

energy. The inherent carbon capture in the CLC reactor system therefore offers a considerable thermodynamic advantage.

There are several works of iron based chemical looping available for hydrogen and electricity co-production [43-45]. Sorgenfrei and TsatsaronisIn [45] used iron oxide ( $\text{Fe}_2\text{O}_3$ ) as oxygen carrier to oxidize the syngas in a multistage moving-bed reactor. The resulting reduced iron particles then consist of  $\text{FeO}$  and  $\text{Fe}_3\text{O}_4$ . To create a closed-cycle operation, these particles are partially re-oxidized with steam in a fluidized-bed regenerator to pure  $\text{Fe}_3\text{O}_4$  and then fully re-oxidized in a fluidized-bed air combustor to  $\text{Fe}_2\text{O}_3$ . One advantage of this process is the co-production of hydrogen diluted with water vapour within the steam regenerator. The option for using  $\text{CO}_2$  turbine and effect of air reactor temperature is also investigated. It was found that the best net efficiency of 43% (based on HHV) can be obtained using a BGL gasifier without a  $\text{CO}_2$  turbine at an air reactor temperature of 1000°C including  $\text{CO}_2$  compression for transport and storage. This is particularly interesting for producing very high purity  $\text{H}_2$  and  $\text{CO}_2$  capture based on fossil fuels conversion without having a huge acid gas removal (AGR) plant based on gas-liquid absorption process.

Petrakopoulou et al. [46] evaluated the CLC technology from an economic and environmental perspective by comparing it with respect to a reference plant, a combined cycle power plant that includes no  $\text{CO}_2$  capture. Two exergy-based methods, the exergoeconomic and the exergoenvironmental analyses, are used to determine the economic and environmental impacts, respectively. As initially intended by the developers of this technology, the combustion process in the CLC unit (reactors) showed lower irreversibilities than that of the conventional combustion chamber of the reference case, due to the nitrogen-free combustion and the preheating of the fuel. Additionally, the overall process results in a relatively low decrease of about 5 percentage points in the exergetic efficiency, with respect to the reference plant. For the plant with CLC, a high increase in the cost of electricity is observed, while at the same time the environmental impact decreases.

The performance of CLC-IGCC can be further increased by the modifications in plant or processes. They are; (1) addition of supplementary firing reactor, to increase the depleted air temperature from air reactor that gives higher efficiency [47]. (2) More than one fuel reactor, to increase the conversion of fuel [47]. (3) Integration of gasification unit with air reactor, that uses the heat released from the process and avoids the need of oxygen for gasification [48]. (4) in-situ CLC, where solid fuels can be sent to the FR directly for power production. So it avoids an external gasification step and reduces the capital cost of plant [49]. (5) ASU (air separation unit)-GT (gas turbine) integration, reduces the power consumption for air compression [42]. Therefore CLC power plant is able to reduce the  $\text{CO}_2$  from the atmosphere on condition of high plant energy efficiency.

## 2. CLC of Gaseous fuels

This section elucidates the fundamentals of the Chemical-Looping Combustion process using metal oxides as oxygen-carriers, being mainly focused in description of results obtained with gaseous fuels.

### 2.1 Process fundamentals

The process is based on the transfer of oxygen from air to the fuel by means of a solid oxygen-carrier avoiding direct contact between fuel and air. Figure 2.1 shows a general scheme of this process. In a first step, the fuel is oxidized to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  by a metal oxide ( $\text{M}_x\text{O}_y$ ) that is reduced to a metal (M) or a reduced form  $\text{M}_x\text{O}_{y-1}$ . If the composition of the fuel gas is expressed as  $\text{C}_n\text{H}_{2m}\text{O}_p$ , the global reduction process is given by reaction (1). The gas produced in this first step contains primarily  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . After water condensation and purification, a highly concentrated stream of  $\text{CO}_2$  ready for transport and storage is achieved. This concept is the main advantage of the process in relation with other  $\text{CO}_2$  capture technologies. In this sense, CLC is a combustion process with inherent  $\text{CO}_2$  separation, i.e. avoiding the need of  $\text{CO}_2$  separation units and without any penalty in energy. The metal or reduced metal oxide is further oxidized with air in a second step, and the material regenerated is ready to start a new cycle (reaction 2). The flue gas obtained contains  $\text{N}_2$  and unreacted  $\text{O}_2$ . The net chemical reaction over the two steps, and therefore the combustion enthalpy, is the same to conventional combustion where the fuel is burned in direct contact with oxygen from air (reaction 3). Therefore, the total amount of heat evolved in the CLC process is the same as in conventional combustion.

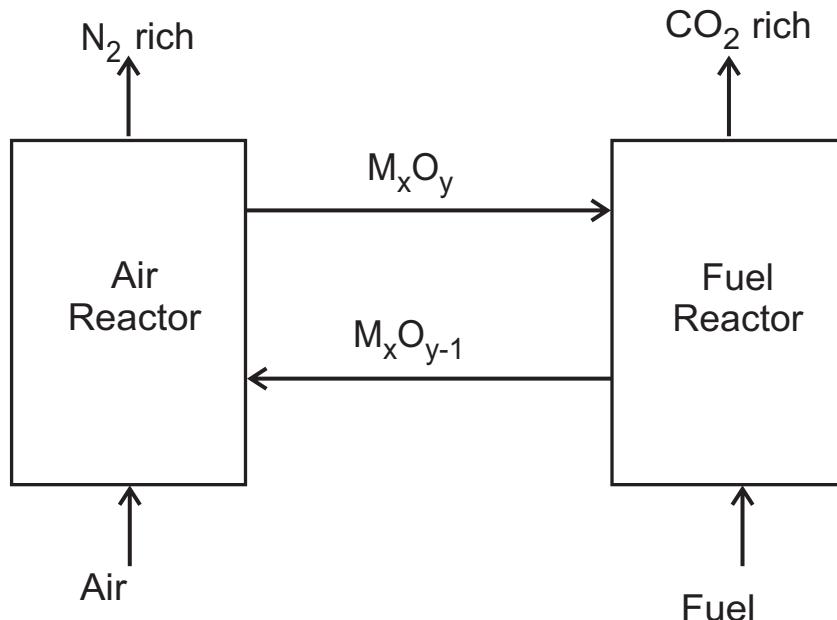
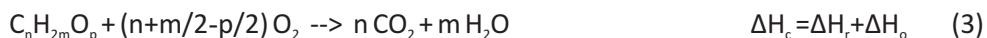
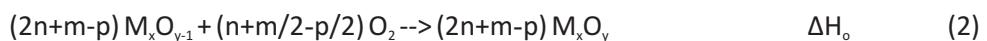


Figure 2.1 General scheme for chemical looping combustion system

The Chemical-Looping concept showed in [Figure 2.1](#) has been proposed to be accomplished in different types of reactors and configurations, namely

- (a) two interconnected moving or fluidized-bed reactors
- (b) alternated packed or fluidized-bed reactors; or
- (c) a rotating reactor.

These designs are discussed in detail in the section 4.

To identify the solid compounds that have the capacity to transfer oxygen in a CLC system is an essential task. To be considered as oxygen-carrier for CLC, a compound must show a favourable tendency toward high conversion of fuel gas to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Jerndal et al. [50] showed a broad thermodynamic analysis of different redox systems considered for CLC. They identified oxides of Cu, Ni, Co, Fe and Mn with favourable thermodynamics for  $\text{CH}_4$ ,  $\text{H}_2$  and CO conversion. At temperatures and pressures relevant for CLC,  $\text{CH}_4$  is not thermodynamically stable and variable amounts of  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , CO, and  $\text{H}_2$  could appear depending on the redox system. Determination of the equilibrium constant for the reduction reaction with  $\text{H}_2$  and CO with different redox systems is needed. Higher equilibrium constant means a higher conversion of the reducing gas. The selectivity towards  $\text{CO}_2$  and  $\text{H}_2\text{O}$  which is affected by the equilibrium constant for CO and  $\text{H}_2$ , respectively depends on the redox system.

## 2.2 Oxygen Carrier (OC) fundamentals

The key issue in the performance of the entire system is the oxygen-carrier material. The oxygen-carrier must accomplish the following characteristics:

- (i) sufficient oxygen transport capacity,
- (ii) favourable thermodynamics regarding the fuel conversion to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in CLC,
- (iii) high reactivity for reduction and oxidation reactions, to reduce the solids inventory in the reactors, and maintained during many successive redox cycles,
- (iv) resistance to attrition to minimize losses of elutriated solids,
- (v) negligible carbon deposition that would release  $\text{CO}_2$  in the air reactor reducing  $\text{CO}_2$  capture efficiency,
- (vi) good fluidization properties (no presence of agglomeration),
- (vii) limited cost,
- (viii) environmental friendly characteristics.

The first two characteristics are intrinsically dependent on the redox system, and they have been analyzed in the previous section. The cost and the environmental characteristics have also relation with the type of metal oxide used. The quality of the other required characteristics must be experimentally determined for each specific material. Normally, the pure metal oxides do not fulfil the above

characteristics and reaction rates quickly decreased in a few cycles [51, 52], showing the need of using a support. A porous support provides a higher surface area for reaction, a binder for increasing the mechanical strength and attrition resistance. In this sense, the method used in the preparation of the materials strongly affects the properties of the oxygen-carrier. The distribution of the metal oxide on the support and the possible interaction between them will affect the oxygen-carrier reactivity, as well as the strength and material stability during the consecutive redox cycles. Several preparation methods can be found in the literature. There are methods in which powders of metal oxide and support are mixed (mechanical mixing and extrusion, freeze granulation, spray drying, or spin flash). In other methods, a solution of the active metal and support are used as original products in the preparation. In this case, the solid compounds are generated by precipitation (co-precipitation, dissolution, sol-gel, solution combustion). Finally, there is the impregnation method where a solution containing the active metal is deposited on a resistant and porous solid support. More specific information about the oxygen-carrier prepared by different methods can be found in the works referenced in the review article [13]. An important feature of the preparation method is the scale up. Most of the preparation methods cited above are developed for laboratory scale production. At the moment, the preparation methods planned for oxygen-carrier preparation at large-scale production are spray drying, spin flash and impregnation. Besides reactivity, other important feature of an oxygen-carrier is the economic cost, especially for synthetic materials. The cost of an oxygen-carrier will be the sum of several factors including the cost of the metal oxide, the inert, and the manufacturing cost. When industrial methods are used, the manufacturing costs of the oxygen-carrier are rather low and the final cost is mainly given by the price of the raw materials. Cobalt and nickel are the more expensive metals, followed by copper. Manganese and iron exhibit the lowest prices.

Abad et al. [53] presented an evaluation of the impact of the cost of the metal oxide on the CO<sub>2</sub> capture cost based on the reactivity and lifetime of the materials. The whole cost of the oxygen-carrier in the process will depend on the lifetime of the particles. Considering the makeup flow of the particles as the main cost associated with the process, a lifetime of the particles of about 300 h represents the same cost of material than the makeup of amine in the commercial MEA absorption technology of post-combustion CO<sub>2</sub> capture. In addition, particles with lifetime under 100 h would fulfil the target range of 20-30\$ per tonne of CO<sub>2</sub> avoided proposed for future CO<sub>2</sub> capture processes. Lifetime values much higher than those have been inferred from several works during long operation in continuous CLC pilot plants [54, 55]. Therefore, it can be concluded that the cost of the particles does not represent a limitation to the technology development [53, 54].

Environmental and health issues must be considered to ensure the process meets future high standards of environmental performance and workplace safety. However, little information has been published related to the possible environment and health problems derived from the use of the above materials in

CLC process. In general, nickel and cobalt are considered the materials exhibiting the highest risk during operation. Emissions containing nickel particles from the air-reactor deserve special attention since nickel derived compounds have carcinogenic properties, and the effects and health impacts on the surroundings have to be considered. Cobalt is also expensive and involves health and safety aspects. On the contrary, iron and manganese are considered as non-toxic materials for CLC applications. The unique work regarding environmental aspects in the handling of materials useful for CLC processes was carried out by García-Labiano et al. [56] who made a study about the solid waste management of a CLC plant using Cu-based oxygen-carriers. They concluded that the solid residue finally obtained after a recovery process can be classified as a stable non reactive waste acceptable at landfills for nonhazardous wastes. Although more work regarding environmental aspects is necessary for the scale-up of CLC technology, it can be said that these aspects have not been identified as immediate showstoppers

### **2.3 Studies on OCs – Ni, Cu, Fe, Mn, Co – based OCs and Mixed oxides**

Many efforts have been made to develop oxygen-carriers suitable for the different processes. A selection of oxygen-carrier materials for natural gas and syngas combustion has been summarized by Lyngfelt et al. [31] and Hossain and de Lasa [32]. Most of the oxygen-carriers proposed in the literature are synthetic materials. The active metal oxides ( $\text{CuO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{NiO}$ ,  $\text{Mn}_3\text{O}_4$  or  $\text{CoO}$ ) are supported on different inert materials such as  $\text{Al}_2\text{O}_3$ ,  $\text{MgAl}_2\text{O}_4$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$  or stabilized  $\text{ZrO}_2$  (with yttria,  $\text{MgO}$  or  $\text{CaO}$ ), bentonite, sepiolite, etc. Major contributors are Chalmers University of Technology (CHALMERS), Institute of Carboquímica belonging to Spanish National Research Council (ICB-CSIC), Tokyo Institute of Technology (TITECH) and Korea Institute of Energy Research (KIER). In addition, on the basis of lower cost with respect to synthetic materials, there are some studies on the suitability of using some minerals as iron ore, ilmenite, manganese ore or waste materials coming from steel industry and alumina production.

Thus, more than 700 carriers have been developed and tested. An overview of the development work on oxygen-carrier materials made in the past, including synthetic materials, mixed oxides, minerals and waste materials can be seen in the review articles [13, 33]. These tables give information about the metal oxide content, support, preparation method, as well as the laboratory installation or facility where it has been tested, the reacting gases and the application for which it has been directed. Similar materials prepared with different metal oxide content or calcination temperatures have been grouped. A compilation of the methods used for oxygen carrier preparation can be found elsewhere [22].

The attrition behaviour of the solids is an important characteristic for its use in fluidized-bed reactors. For this purpose, crushing strength of the oxygen-carrier is a preliminary indicator. Standard test for attrition behaviour of fluidizable solid give a more relevant indication because conditions are relevant for industrial operation [57]. However it is necessary to consider that chemical stress due to redox

reactions is present together with physical attrition effects. Thus attrition behaviour obtained during multicycle redox reactions in a batch fluidized bed or in a continuously operated CLC unit is a good indicator of the expected behaviour in a CLC system.

Lifetime of oxygen-carriers is an important parameter to be evaluated at full scale. The lifetime of the oxygen-carriers can be defined as the mean time that a particle must be under reaction (reduction or oxidation) in the system without any reactivity loss or without suffering the attrition/fragmentation processes that produce particle elutriation out of the system. Normally, loss of fines is defined as the loss of particles smaller than 45 mm [54]. It is assumed that particles of this size have a short residence time in a commercial unit and thus are of little use in the process. To determine their value with accuracy, operation in continuous CLC units during long time periods is necessary. The economical cost of the makeup stream of solids to replace loss of fines will depend on the lifetime of particles and on the cost of the oxygen-carrier, which is mainly affected by the metal used and its content in the solid.

**Table 3** shows the lifetime data available in literature during long time tests in continuous units. The highest experience corresponds to Ni-based oxygen-carriers. High lifetime values were derived for these particles. It must be remarked that the lifetime of particles prepared by spray drying and a total NiO content about 60 wt% was 33000 h [58], which was calculated from extrapolation of data obtained during 1016 h of continuous operation. Lower lifetime values have been obtained for NiO/NiAl<sub>2</sub>O<sub>4</sub> particles prepared by spin flash or for impregnated Cu-based materials. Investigations to obtain high resistant copper particles to operate at high temperature gave lifetime values up to 2700 h [59] for impregnated particles with 13 wt% CuO and 3 wt% NiO.

An important aspect of the oxygen-carrier materials is the suitability to be used in continuous CLC units during long periods of time. However, the number of materials tested in this kind of units is limited. **Table 4** shows a summary of those oxygen-carriers tested in continuous CLC units specifying the operation time of each material. In short, **Table 5** shows a summary of the operation hours in continuous plant depending on the metal oxide, and application for the works published up to the end of 2010.

Table-3 Lifetime of oxygen carriers based on attrition data [58]

| Carrier   | Facility                | Operation time (h) | T (°C) |      | Attrition rate (%/h) | Lifetime (h) |
|---|-------------------------|--------------------|--------|------|----------------------|--------------|
|   |                         |                    | FR     | AR   |                      |              |
| NiO/Al <sub>2</sub> O <sub>3</sub>                                      | CLC 10 kW <sub>th</sub> | 100                | =900   | 1000 | 0.0023               | 40000        |
| NiO/NiAl <sub>2</sub> O <sub>4</sub> + MgAl <sub>2</sub> O <sub>4</sub> | CLC 10 kW <sub>th</sub> | 1016               | =940   | 1000 | 0.003                | 33000        |
| NiO/NiAl <sub>2</sub> O <sub>4</sub>                                    | CLC 10 kW <sub>th</sub> | 160                | =940   | 1000 | 0.022                | 4500         |
| NiO/α-Al <sub>2</sub> O <sub>3</sub>                                    | CLC 500 W <sub>th</sub> | 70                 | 880    | 950  | 0.01                 | 10000        |
| CuO / γ-Al <sub>2</sub> O <sub>3</sub>                                  | CLC 10 kW <sub>th</sub> | 100                | 800    | 800  | 0.04                 | 2400         |
| CuO/γ-Al <sub>2</sub> O <sub>3</sub>                                    | CLC 500 W <sub>th</sub> | 60                 | 800    | 900  | 0.09                 | 1100         |
| CuO/NiO-Al <sub>2</sub> O <sub>3</sub>                                  | CLC 500W <sub>th</sub>  | 67                 | 900    | 950  | 0.04                 | 2700         |
| Iron ore  | CLCs 1 kW <sub>th</sub> | 10                 | 950    | 1010 | 0.0625               | 1600         |

## Developments in Chemical Looping Technology Worldwide

**Table-4: Summary of the Oxygen carriers tested in continuously operated CLC and CLR units**

| Metal oxide 1 (wt%)          | Metal oxide 2 (wt%) | Support material                     | Preparation method | Application and facility   | Reacting gas  | Operation time (h) <sup>2</sup>             |
|------------------------------|---------------------|--------------------------------------|--------------------|--|---|---|
| NiO18                        |                     | $\alpha\text{-Al}_2\text{O}_3$       | IMP                | CLC 300 W<br>CLC 500 W<br>CLC 500 W<br>CLC 500 W<br>CLC 500 W<br>CLR 500 W<br>CLR 900 W          | n.g.<br>$\text{CH}_4$<br>$\text{H}_2, \text{CO}$ , syngas<br>$\text{C}_2\text{H}_6, \text{C}_3\text{H}_8$<br>$\text{CH}_4 + \text{H}_2\text{S}$<br>n.g.<br>$\text{CH}_4 + \text{H}_2\text{O}$ | 41<br>70<br>50<br>40<br>45<br>36<br>40      |
| 21                           |                     | $\gamma\text{-Al}_2\text{O}_3$       | IMP                | CLC 300 W<br>CLR 500 W<br>CLR 900 W  | n.g.<br>n.g.<br>$\text{CH}_4 + \text{H}_2\text{O}$  | 5<br>37<br>40                               |
| 35                           |                     | $\text{Al}_2\text{O}_3$              | COP                | CLC 1 kW<br>CLCs 1 kW<br>CLCs 10 kW  | Syngas + $\text{H}_2\text{S}$<br>Coal<br>Coal   | n.a.<br>30<br>100                           |
| 32.7                         |                     | $\text{NiAl}_2\text{O}_4$            | IMP                | CLCs 10 kW   | Coal  | 30  |
| 60                           |                     | $\text{NiAl}_2\text{O}_4$            | FG                 | CLC 300 W  | n.g.  | 8   |
| 60                           |                     | $\text{NiAl}_2\text{O}_4$            | FG                 | CLC 10 kW  | n.g.  | 100   |
| 40                           |                     | $\text{NiAl}_2\text{O}_4$            | SD                 | CLC  | $\text{H}_2$  | n.a.  |
| 40                           |                     | $\text{NiAl}_2\text{O}_4$            | SD                 | CLC 300 W<br>CLC 10 kW<br>CLC 120 kW<br>CLC 120 kW   | n.g.<br>$\text{H}_2, \text{CO}$<br>n.g.<br>$\text{CH}_4$  | 60<br>n.a.<br>90<br>n.a.                    |
| 40                           |                     | $\text{NiAl}_2\text{O}_4\text{-MgO}$ | SD                 | CLC 300 W<br>CLC 10 kW<br>CLC 120 kW<br>CLR 140 kW   | n.g.<br>n.g.<br>n.g.<br>n.g.  | 40<br>611 <sup>b</sup><br>90<br>18          |
| 20                           |                     | $\text{MgAl}_2\text{O}_4$            | FG                 | CLC 300 W<br>CLR 500 W   | n.g.<br>n.g.  | 10<br>49                                    |
| 60                           |                     | $\text{MgAl}_2\text{O}_4$            | FG                 | CLC 300 W<br>CLC 170 W<br>CLR 500 W  | n.g.<br>Syngas<br>n.g.  | 30<br>30<br>40                              |
| 60                           |                     | Bentonite                            | MM                 | CLC 50 kW  | $\text{CH}_4$<br>Syngas   | 3.5<br>53                                   |
| 60                           |                     | Bentonite                            | MM                 | CLC 1.5 kW   | $\text{CH}_4$   | n.g.  |
| 40                           |                     | $\text{ZrO}_2\text{-MgO}$            | FG                 | CLC 300 W<br>CLR 500 W   | n.g.<br>n.g.  | 16<br>24                                    |
| OCN702-1100                  |                     | n.g.                                 | SD                 | CLC 50 kW  | n.g.  | n.a.  |
| OCN703-1100                  |                     | n.g.                                 | SD                 | CLC 50 kW  | n.g.<br>Syngas  | 53<br>52                                    |
| CuO                          |                     |                                      |                    |  |   |   |
| 15                           |                     | $\alpha\text{-Al}_2\text{O}_3$       | IMP                | CLC 500 W  | $\text{CH}_4$   | 30  |
| 14                           |                     | $\gamma\text{-Al}_2\text{O}_3$       | IMP                | CLC 10 kW<br>CLC 500 W<br>CLC 500 W<br>CLC 500 W<br>CLC 500 W<br>CLC 500 W                       | $\text{CH}_4$<br>$\text{H}_2, \text{CO}$ , syngas<br>$\text{CH}_4, \text{H}_2\text{S}$<br>$\text{CH}_4, \text{HC}$<br>$\text{CH}_4$<br>$\text{CH}_4$  | 120<br>40<br>32<br>30<br>50<br>89           |
| 12                           |                     | $\text{MgAl}_2\text{O}_4$            | IMP                | CLC 500 W  | $\text{CH}_4$   | 50  |
| $\text{Fe}_2\text{O}_3$      |                     |                                      |                    | CLCs 10 kW   | Biomass   | 30  |
| Pure                         |                     |                                      |                    | CLC 300 W  | PSA-offgas  | 40  |
| 20                           |                     | $\text{Al}_2\text{O}_3$              | IMP                | CLC 300 W  | n.g. syngas   | 40  |
| 60                           |                     | $\text{Al}_2\text{O}_3$              | FG                 | CLC 300 W  | $\text{CH}_4$   | n/a   |
| 60                           |                     | Bentonite                            | MM                 | CLC 1 kW   | n.g.  | 17  |
| n.a.                         |                     | n.a.                                 | n.a.               | CLC 10 kW  | n.g.  |   |
| $\text{Mn}_3\text{O}_4$      |                     |                                      |                    |  |   |   |
| 40                           |                     | $\text{Mg-ZrO}_2$                    | FG                 | CLC 300 W  | n.g. syngas   | 70  |
| $\text{Co}_3\text{O}_4$      |                     |                                      |                    |  |   |   |
| n.a.                         |                     | $\text{CoAl}_2\text{O}_4$            |                    | CLC 50 kW  | n.g.  | 25  |
| Mixed oxides                 |                     |                                      |                    |  |   |   |
| CuO (13)                     | NiO (3)             | $\gamma\text{-Al}_2\text{O}_3$       | IMP                | CLC 500 W  | $\text{CH}_4$   | 67  |
| $\text{Fe}_2\text{O}_3$ (45) | CuO (15)            | $\text{MgAl}_2\text{O}_4$            | MM                 | CLCp 10 kW   | Coke oven gas   | 15  |
| $\text{Fe}_2\text{O}_3$ (45) | NiO (15)            | Bentonite                            | MM                 | CLC 1 kW   | $\text{CH}_4$   | n.a.  |
| $\text{Fe}_2\text{O}_3$ (30) | NiO (30)            | Bentonite                            | MM                 | CLC 1 kW   | $\text{CH}_4$   | n.a.  |
| $\text{Fe}_2\text{O}_3$ (15) | NiO (45)            | Bentonite                            | MM                 | CLC 1 kW   | $\text{CH}_4$   | n.a.  |
| Low cost materials           |                     |                                      |                    |  |   |   |
| Ilmenite (Norway)            |                     |                                      |                    | CLCs 500 W<br>CLCs 10 kW<br>CLCs 10 kW<br>CLCs 120 kW<br>CLC 1.3 kW<br>CLCs 1 kW<br>SR-CLC 500 W | coal<br>pet-coke<br>coal<br>n.g. syngas<br>syngas<br>coal<br>$\text{CH}_4$ , syngas, PSA-offgas   | 26<br>30<br>22<br>n.a.<br>n.a.<br>10<br>111 |
| Ilmenite (Australia)         |                     |                                      |                    |  |   |   |
| Iron Ore (Australia)         |                     |                                      |                    |  |   |   |
| Redmud                       |                     |                                      |                    |  |   |   |

<sup>a</sup> The operation time corresponds to the period with fuel feedings.

<sup>b</sup> Partially mixed with NiO/NiAl<sub>2</sub>O<sub>4</sub> particles (included in 1016 h in the above carrier)

Table-5: Summary of the experience time (in hours) on CLC and CLR in continuous units.

| Oxygen Carriers    | CLC  | CLC(solid) | CLR | Total |
|--------------------|------|------------|-----|-------|
| Nickel             | 2114 | 160        | 284 | 2558  |
| Copper             | 391  | -          | -   | 391   |
| Iron               | 97   | 30         | -   | 127   |
| Manganese          | 70   | -          | -   | 70    |
| Cobalt             | 25   | -          | -   | 25    |
| Mixed oxides       | 82   | -          | -   | 82    |
| Low cost materials | 111  | 88         | -   | 199   |
| Total              | 2890 | 278        | 284 | 3452  |

### Ni-based OCs

Ni-based OCs have all the desirable characteristics for CLC mainly because they can operate at high temperatures ( $> 900^{\circ}\text{C}$ ) and have good methane conversion rates. The disadvantage is that Ni is conducive to the formation of CO and  $\text{H}_2$ .

It is widely observed that NiO supported over an inert material has higher reactivity and mechanical strength than pure NiO. Examples of support materials include Yttria-stabilized-Zirconia (YSZ),  $\text{Al}_2\text{O}_3$ ,  $\text{NiAl}_2\text{O}_4$ ,  $\text{MgAl}_2\text{O}_4$ , oxides of Si, Ti, Zr and so on. Of these, NiO coated with  $\text{NiAl}_2\text{O}_4$  has the highest potential to be an OC for a CLC process for applications using natural gas or syngas as the fuel because of its high reactivity in oxidation and reduction, high selectivity of  $\text{CH}_4$  to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  and high mechanical strength and durability over a wide temperature range. It is relatively inexpensive too.

### Cu-based OCs

$\text{CuO}/\text{Cu}$  has the advantage of having the highest oxygen carrying capacity among the metal oxides. High  $\text{O}_2$ -carrying capacity leads to low solids flow rate. Its reduction reaction with fuel is also exothermic which means that no additional heat is required for the reaction to take place. Thermodynamically also,  $\text{CuO}/\text{Cu}$  is favored for complete conversion in the reduction reaction. Besides, Cu is one of the cheapest metals. However, reactivity of this metal oxide reduces after a few cycles and it cannot operate at high temperatures.

In order to improve the reactivity of  $\text{CuO}/\text{Cu}$  systems,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  have been tried as binder materials. Though reactivity can be improved, high-temperature operation still is an area of concern.

### Fe-based OCs

Iron oxides are abundantly available in nature in various forms – magnetite ( $\text{Fe}_3\text{O}_4$ ), hematite ( $\text{Fe}_2\text{O}_3$ ) and wustite ( $\text{FeO}$ ). Hence, iron based oxygen carriers have high environmental compatibility. Because of their abundance, their prices are lower than the oxides of Cu or Ni. Of these,  $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$  combination has the fastest reduction rate, and hence is more favored than  $\text{Fe}_3\text{O}_4/\text{FeO}$  or  $\text{FeO}/\text{Fe}$  combinations.

Though pure  $\text{Fe}_2\text{O}_3$  has excellent chemical stability at lower temperatures ( $<800^\circ\text{C}$ ), it is prone to agglomeration at higher temperatures. Addition of supports such as  $\text{Al}_2\text{O}_3$  and  $\text{MgAl}_2\text{O}_4$  improves reactivity and mechanical strength but there is scope for further improvement in high-temperature operation.

However,  $\text{Fe}_2\text{O}_3$  can be used as an oxygen carrier for CLC of solid fuels like coal because it enhances gasification reactions, which need to occur before the actual combustion begins.

### **Mn-based**

Though it is a promising metal oxide, it has not been widely tested so far. The disadvantage of manganese oxides is their incompatibility with common support materials like  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ . But  $\text{Mn}_2\text{O}_3$  with  $\text{ZrO}_2$  as the support material has very high reactivity and mechanical strength. Its feasibility as an oxygen carrier will be known only after wide-scale testing.

Based on the above brief description, Ni-based oxygen carriers are likely to be favored for gaseous fuel CLC.

### **Mixed metal oxides**

Mixed metal oxides, which are a combination of oxides of two or more metals, are novel materials which aim to avoid the disadvantages and combine the advantages of individual metal oxides. For example, though  $\text{CuO}$  cannot operate at high temperatures and  $\text{NiO}$  leads to the formation of  $\text{CO}$  and  $\text{H}_2$  in the products, the combination of  $\text{CuO}$  and  $\text{NiO}$  can be operated at high temperatures without  $\text{CO}$ -formation. Though mixed metal oxides have not been widely tested, they do have potential to become efficient oxygen carriers for CLC.

### **Others**

Besides the metal oxides discussed above, other oxygen carriers have also been tried for their applicability to CLC.

Perovskites are materials in which metal oxides are combined in a non-stoichiometric ratio, thereby introducing structural and electronic defects that can be used to enhance reactivity. Though some of them (eg.  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.2}\text{O}_{3-\delta}$ ) have been tested, a lot of improvement is still needed for them to be used as oxygen carriers for CLC.

$\text{CaSO}_4$  has also been tried as an oxygen carrier. Though it exhibits good reactivity and stability, the formation of  $\text{SO}_2$  at high temperatures is a definite disadvantage.

## 2.4 Studies on effect of fuel gas composition

Several gases have been considered as potential fuels for CLC including natural gas, refinery gas or syngas from coal gasification. Commonly, the investigations are carried out with synthetic gases simulating the composition of these fuels. However, real fuel gases contain variable amounts of light hydrocarbons (LHC), i.e. C<sub>2</sub>-C<sub>5</sub>, and sulfur compounds, such as H<sub>2</sub>S, COS, mercaptans, and thioaromatics. These compounds can produce strong environmental and operational problems, which will affect the design of the CLC plant. This problem is also maintained in the most recent application of CLC with solid fuels, some of them characterized by their high sulfur content.

Recently, biogas generated from municipal solid waste, wastewater, animal manure and agricultural wastes has been also considered as an option to be used in a CLC process [60]. Moreover, the application of CLC for heat production from liquid fuels such as heavy hydrocarbons proceeding from oil and refinery industry has been also established [61]. The use of liquid fuels raises specific problems of implementation in an industrial plant that are very different from the extensively studied gaseous and solid fuels. However, the research on liquids fuels is in a very initial stage of development.

### Sulfur

Usually all fuels (natural gas, syngas, refinery gases and coal) contain sulfur compounds in variable amounts. Natural gas contains very small amounts of H<sub>2</sub>S (=20 vppm). H<sub>2</sub>S content in refinery fuel gas can vary depending on the site but contents up to 800 vppm can be found, and this value can be increased up to 8000 vppm for raw syngas obtained from coal gasification [62]. The design of an industrial CLC plant can be affected by the presence of these sulfur compounds in a double way, and depending on the oxygen-carrier used. From the environmental point of view, the sulfur fed into the system can be released as SO<sub>2</sub> in the air-reactor gas outlet stream and must fulfil the legislation about gaseous emissions, or be emitted in the fuel-reactor gas stream affecting the quality of the CO<sub>2</sub> with important consequences for the compression, transport and storage [63, 64]. Pipitone and Bolland [65] give some examples of quality specifications for CO<sub>2</sub> transport and storage of some industrial companies operating at the moment.

From an operational point of view, the sulfur compounds may react with the active metal oxide to form several metal sulphides that are poisonous to the oxygen-carrier, decreasing their reactivity. This process is especially important when Ni-based oxygen-carriers are used [66]. Moreover, the low melting point of some sulphides could produce agglomeration and affect the solids circulation pattern between the interconnected fluidized-bed reactors [67].

Several works have shown thermodynamic calculations about the fate of H<sub>2</sub>S in a CLC process depending on the metal oxide selected as oxygen-carrier, the operating conditions (temperature, pressure, and H<sub>2</sub>S concentration), and the fuel gas (CH<sub>4</sub>, CO or H<sub>2</sub>). Mattisson et al [67] carried out a thermodynamic study

about the fate of H<sub>2</sub>S in a CLC system using a Ni-based oxygen-carrier and CH<sub>4</sub> as fuel. They found that H<sub>2</sub>S may be oxidized to SO<sub>2</sub> in the fuel reactor by oxidants such as H<sub>2</sub>O, CO<sub>2</sub> and even the NiO. The degree of conversion to SO<sub>2</sub> is enhanced at high temperatures and low pressures. Both SO<sub>2</sub> and H<sub>2</sub>S could react with the active metal (NiO or Ni) to form sulphides or sulphates (NiS, NiS<sub>2</sub>, Ni<sub>3</sub>S<sub>2</sub> or NiSO<sub>4</sub>). They found out that NiSO<sub>4</sub> is not formed at the conditions which may be encountered in the fuel-reactor, and Ni<sub>3</sub>S<sub>2</sub> was the thermodynamically most stable sulphide. Jerndal et al [50] and Wang et al [68] carried out a thermodynamic investigation about carbon deposition and sulfur evolution in CLC for most of the metal oxides used as oxygen-carriers and several fuel gases. They detected several sulphides (Ni<sub>3</sub>S<sub>2</sub>, Fe<sub>0.84</sub>S, CoS<sub>0.89</sub>) as the most possible solid sulfur compounds that can be formed at partial pressures and temperatures which may be encountered in a CLC fuel-reactor. For CuO, the Cu<sub>2</sub>S was the most thermodynamically favored under oxygen-deficient conditions. MnSO<sub>4</sub>, instead of sulphides, was found as the predominant solid species for Mn-based as oxygen-carrier, at both oxidizing and reducing conditions. Tian et al.[69] have carried out a thermo gravimetric study about the effect of H<sub>2</sub>S present in syngas on the behaviour of several bentonite-supported metal oxides based on iron, nickel, manganese and copper during 10 redox cycles. They found that the rates of reduction and oxidation decreased in the presence of H<sub>2</sub>S for all four metal oxides, with the highest decrease for NiO and the lowest for Mn<sub>2</sub>O<sub>3</sub>. It must be noted that the thermodynamic analysis considers the final condition reached at equilibrium. However the results are difficult to extrapolate to a flow reactor with continuously changing conditions and with kinetic constraints. Therefore, experimental data are necessary to know the real consequences in a CLC process. However, only few studies have been made in continuous units to analyze the effect of sulfur using NiO and CuO oxygen-carriers under different operating conditions.

### 3. CLC of Solid fuels

Chemical-Looping Combustion (CLC) with gaseous fuels has been developed in the last years, but CLC with solid fuels has recently gained a great interest. The use of coal in CLC is very attractive in the future sceneries with restriction in CO<sub>2</sub> emissions, since coal will be the main energy source in the medium term. In addition, other solid fuels could be used in a CLC system, as pet-coke, solid wastes or biomass. In the case of using biomass as fuel, the CO<sub>2</sub> captured can be considered as a negative emission because this CO<sub>2</sub> was already removed from atmosphere through a photosynthesis process in the plants. In this section, different options to process solid fuels in a CLC system are described. In each case, the specific way in which the solid fuel is being converted will determine the design of the CLC system, as well as the selection of the suitable oxygen-carrier material.

As shown in Figure 3.1, there are two approaches for the use of the CLC technology with coal. The first one is to first carry out coal gasification and subsequently to introduce the syngas produced in the CLC

system [14,70,71], i.e. the syngas fuelled CLC (syngas-CLC). The second approach is the direct feeding of the solid fuel to the fuel reactor in a CLC process (solid fuelled-CLC). In this last case two options have been proposed for CLC with solid fuels. On the one hand, the solid fuel is gasified in-situ by  $H_2O$  or  $CO_2$  supplied as fluidization agent [72], i.e. the in-situ Gasification Chemical-Looping Combustion (iG-CLC). On the other hand, Mattisson et al. [20] proposed the so-called Chemical-Looping with Oxygen Uncoupled (CLOU) process, where the solid fuel is burned with gaseous oxygen released by the oxygen-carrier in the fuel-reactor.

The main reactions involved in each process are depicted in Figure 3.2. When the coal is previously gasified, the fuel-reactor is fed by syngas, mainly composed of CO and  $H_2$  as reducing agents. In this case, the CLC design should be similar to that for any gaseous fuel, such as natural gas. In the iG-CLC, prior to reaction with the oxygen-carrier, the solid fuel is devolatilized and gasified by  $H_2O$  or  $CO_2$  or both in the fuel-reactor. These gases may be used as fluidizing gas in the fuel-reactor. Eventually, volatiles and gasification products react with the oxygen-carrier particles to produce the combustion products, i.e.  $CO_2$  and  $H_2O$ . Lastly, the CLOU process is characterized by the use of an oxygen-carrier that evolves gaseous oxygen in the fuel-reactor environment. The subsequent combustion of coal is similar to that for normal combustion with air.

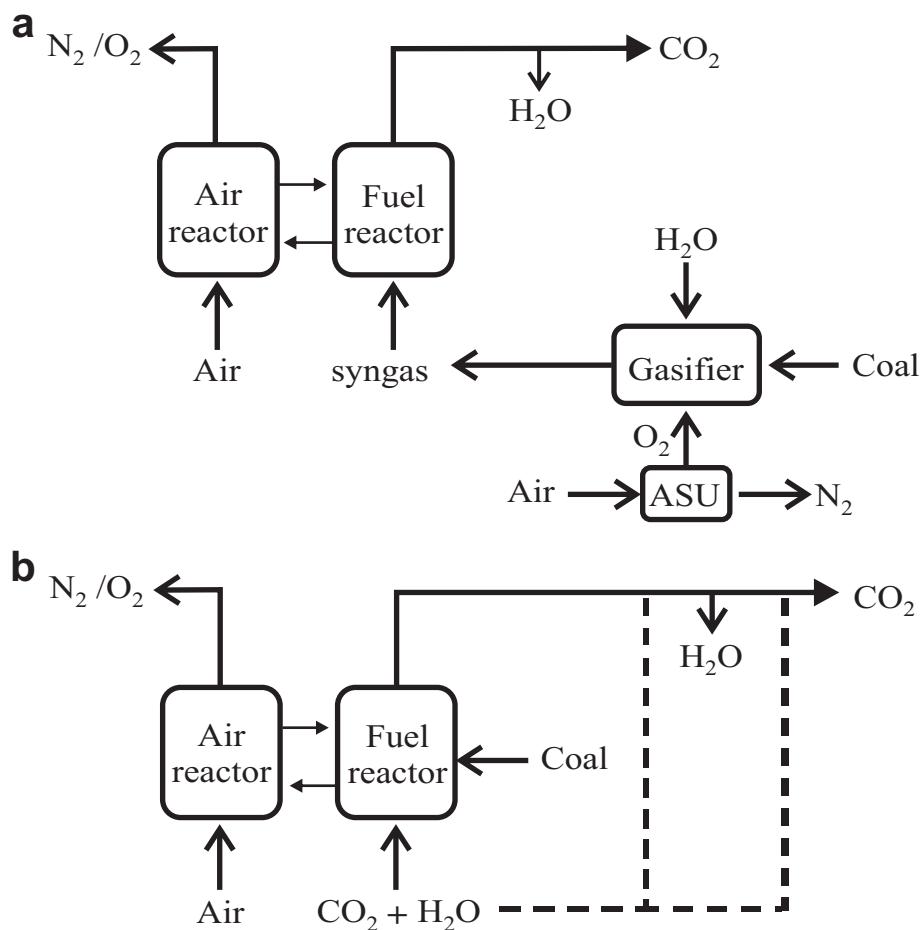


Figure 3.1 Schematic layout of alternatives to process solid fuels in a CLC system (a) previous gasification of the solid fuel (syngas-CLC) and (b) feeding of solid fuel to the fuel reactor (solid fuelled-CLC)

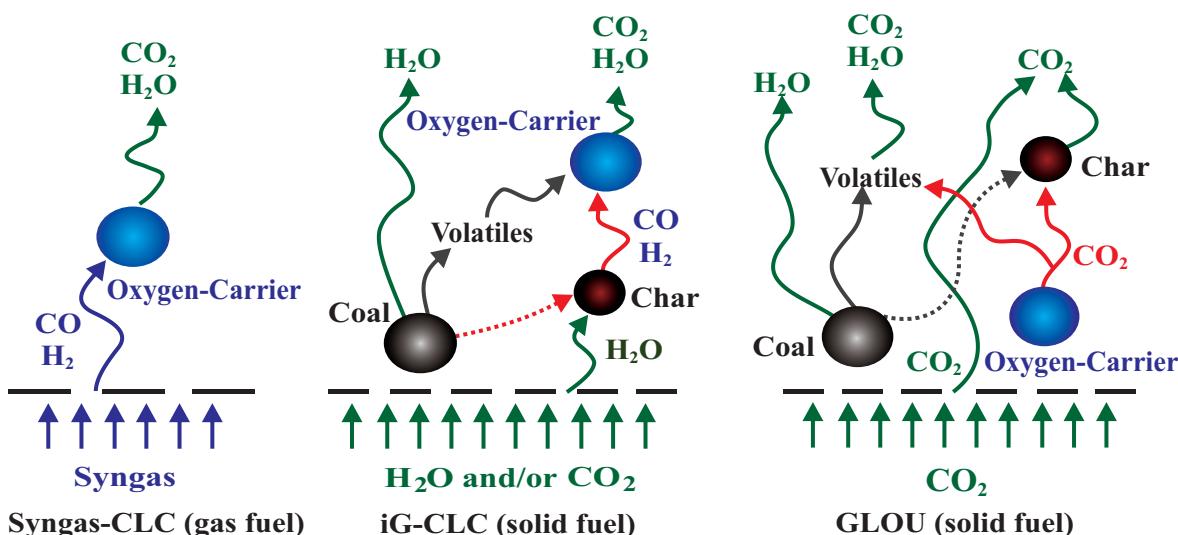


Figure 3.2 Main processes involved in fuel reactor for the three different options proposed for solid fuel processing in a CLC system

### 3.1. Syngas fuelled Chemical-Looping Combustion (Syngas-CLC)

This way to process a solid fuel in a CLC system is schematized in Figure 3.1a. In this case, the solid fuel is gasified to produce a syngas which is fed to the fuel-reactor. To supply the energy required for the endothermic gasification process, oxygen must be used as gasifying agent to ensure that nitrogen is not present together with the  $\text{CO}_2$  stream. Another approach is to supply the energy directly from the CLC system, e.g. introducing the gasifier inside the air reactor [48], with the corresponding heat transfer difficulties between these reactors.

As syngas is a gaseous fuel, benefits of the experience gained using natural gas as fuel can be taken. In this option, a highly reactive synthetic oxygen-carrier is preferred in order to decrease the solids inventory in the CLC system. Several synthetic oxygen carriers based on Ni, Cu, Fe and Mn oxides have shown good reactivity with syngas components, i.e.  $\text{H}_2$  and CO, at atmospheric [73, 74] and pressurized conditions [75-77]. Special care must be taken on sulphur in the syngas, especially for Ni-based oxygen-carriers due to partial deactivation of the material by  $\text{H}_2\text{S}$  [69].

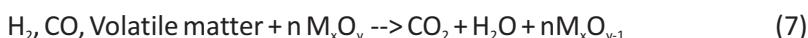
The use of syngas in a CLC system has been successfully accomplished in 300-1000Wth continuous CLC units using Ni-, Cu and Mn-based oxygen-carriers [78-83]. Lower conversion was obtained for an iron on alumina oxygen-carrier [79]. In addition, the use of natural ores or industrial waste has also been suggested as oxygen-carriers for syngas combustion [84-86]. Worse performance was obtained processing syngas in a 120 kWth facility with a natural ilmenite than using a Ni-based oxygen-carrier [87], but the low price and the environmental friendly behaviour of ilmenite are the main reasons to be considered as oxygen-carrier. Lower reactivity was found for  $\text{CaSO}_4$  based oxygen-carriers [88].

Integrating the coal Gasification, CLC and gas turbine Combined Cycle, the process namely ICLC-CC, would have similar efficiencies as the system with conventional IGCC application [48, 89] but without CO<sub>2</sub> capture. As the separation of CO<sub>2</sub> is expected to substantially decrease the net power efficiency in an IGCC system, the CLC systems have a potential of being more efficient. Hence, an additional gain of 5-10% points can be achieved compared to conventional IGCC with CO<sub>2</sub> recovery [77]. However, the ICLC-CC process includes the use of interconnected pressurized Chemical-Looping reactors, which is currently a challenge for the development of this technology.

### **3.2 *in-situ* Gasification CLC (iG-CLC)**

The second approach for the use of coal in CLC is the direct gasification of the solid fuel in the CLC process avoiding the need of a gasifier and the corresponding gaseous oxygen requirement [16,90,91]. The general scheme for the iG-CLC configuration is shown in Figure 3.1b. In this option, the solid fuel is physically mixed with the oxygen-carrier in the fuel-reactor and the carrier reacts with volatiles and the gas products from char gasification, where H<sub>2</sub> and CO are the main components. The fuel-reactor is fluidized by H<sub>2</sub>O, CO<sub>2</sub> or mixtures of these gases, which act as gasifying agents. If CO<sub>2</sub> is used, the energy required for steam production is avoided. CO<sub>2</sub> can be re-circulated from the flue gases. The use of CO<sub>2</sub> has been proposed for highly reactive solid fuels, such as low-rank coals or biomass [92]. Otherwise, special considerations should be given when using CO<sub>2</sub> as gasification agent depending on the design configuration because of the slow gasification rate with CO<sub>2</sub>. To reduce the external energy requirements for the steam generation, coal slurry instead of dry coal particles has been proposed to be introduced into the fuel-reactor [93]. In this way the pyrolysis and gasification of coal is enhanced by the intense exchange of heat and mass when the coal slurry is in contact with the hot oxygen-carrier. However, the solids recirculated from the air-reactor must transport an additional energy to vaporize the water coming with the coal slurry stream.

In the iG-CLC, the solid fuel gasification proceeds first according to reactions (4-6) and the resulting gases and volatiles are oxidized through reduction of the oxidized oxygen-carrier, M<sub>x</sub>O<sub>y</sub>, by means of reaction (7). The water-gas shift (WGS) equilibrium (reaction (8)) can also affect the gas composition obtained in the reactor [94]. The oxygen-carrier reduced by volatiles and gasification products, M<sub>x</sub>O<sub>y-1</sub>, is oxidized with oxygen from air following reaction (9). Thus the oxygen-carrier is regenerated to start a new cycle. The net chemical reaction is the same as in usual combustion with the same combustion enthalpy.



Initial calculations have shown that the iG-CLC process has the potential to obtain higher power efficiencies and lower costs than other evaluated technologies [12], with a net efficiency of the process of about 41-42% [95, 96]. To increase the energy efficiency, the iG-CLC process can be performed at pressurized conditions. The effect of pressure on oxygen-carrier and char reactivity can be very important [94]. On the one hand, an increase of pressure does not lead to the expected increase in reaction rates of the oxygen-carrier [76]. On the other hand, the char gasification rate increase with pressure is not relevant above a certain pressure [97, 98].

Two different iG-CLC concepts have been proposed. Most of the works demonstrating the iG-CLC technology have been carried out using two interconnected fluidized-bed reactors [17, 99, 100]. Another alternative is to use a batch of an appropriate oxygen carrier in a single fluidized bed with three stages [101, 102]. The process would consist of several fluidized-bed reactors operating in parallel and out of phase with one another to achieve a continuous supply of energy. The number of reactors could be high to avoid instabilities from unsteady state operation. The benefits of circulating fluidized-bed technology commonly used in CLC are the fuel flexibility associated with current CFB boilers and that they operate at steady-state, thus supplying energy continuously. Thus, different solid fuels could be used such as coal, pet-coke, biomass or solid wastes [103]. Most of the work found in the literature refers to the use of coal or petcoke as fuels. On the other hand, biomass has been shown to have a relatively fast conversion rate [102-104]. The use of biomass in a continuously operated CLC system has been recently studied [105], showing promising results for further development of a biomass fuelled CLC system. Figure 3.3 shows a general scheme of the iG-CLC system using two interconnected fluidized-bed. Thus, reactions (4-7) proceed in the fuel-reactor, i.e. the solid fuel devolatilization and gasification, as well as subsequent oxidation of the gases generated. The reduced oxygen-carrier from the fuel-reactor,  $M_xO_{y-1}$ , is transferred to the air-reactor where it regenerates its lost oxygen by reacting with oxygen in air which is then transferred to the fuel reactor and start a new cycle.

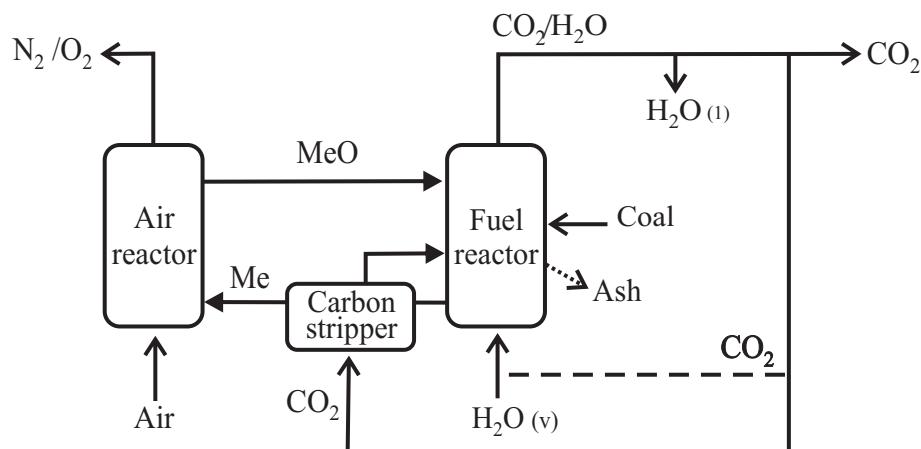


Figure 3.3 Reactor scheme of the iG-CLC process for solid fuel using two interconnected fluidized bed reactors

Ideally, the CO<sub>2</sub> capture is inherent to this process, because the air is never mixed with the fuel, and no additional costs or energy penalties for gas separation are required, as was the case for gaseous fuels. However, the CO<sub>2</sub> capture efficiency can be reduced if some char particles are by-passed to the air-reactor. The gasification process has been identified as the controlling step in the iG-CLC concept [106, 107]. Indeed, the char gasification is usually a slow process, and the solids stream exiting from the fuel-reactor could contain some unconverted char together with the oxygen carrier and ash. Thus, char particles need a long enough residence time in the fuel-reactor to be gasified. To increase the residence time of char particles in the fuel-reactor, without excessive increase of the reactor size, several options can be found:

When using solid fuels, the reaction between the oxygen-carrier and the char remaining after volatiles release is not direct, but involves an intermediate gasification step. This is decisive for the fuel reactor design and the following key targets have been identified in relation to fuel reactor performance:

- High solid fuel conversion, i.e. minimizing loss of unconverted char with flue gas.
- High gas conversion, i.e. minimizing unconverted gases like H<sub>2</sub>, CO and CH<sub>4</sub>.
- High CO<sub>2</sub> capture, i.e. minimizing loss of char to air reactor.

As compared to gaseous fuels, CLC with solid fuels will require a different design of the fuel reactor, as well as oxygen carriers with other properties:

- The ash, normally being part of solid fuels, will make a very long lifetime of the oxygen carrier unlikely, as the ash removal inevitably causes losses of oxygen carrier. Also, the ash might directly affect the oxygen carrier. This means that oxygen carriers should have low cost.
- The gasification of char is a slow process, which means that the fuel reactor needs a design that provides sufficient residence time, in order to avoid char particles reaching the air reactor. Char burning in the air reactor should be avoided, as it will produce CO<sub>2</sub> that will not be captured.
- In order to achieve high conversion of the volatiles, the fuel needs to be fed to the fuel reactor in a way that allows good contact between bed material and the volatiles released.

An advantage for CLC with solid fuels is that most oxygen carriers, including low-cost materials, are highly reactive towards the syngas released from gasification. However, the syngas is released from char particles inside the fuel reactor, in contrast to gaseous fuels which are introduced from below. Thus, some of the syngas released, e.g. in the upper regions, will have insufficient contact with the bed material. Thus, complete conversion of the gas is difficult to obtain.

However, the CO and H<sub>2</sub> from char gasification are not the only gases that need to be converted. The release of volatiles also involves hydrocarbons such as methane which normally is less reactive towards low-cost oxygen carriers. Measures to reach complete or very high conversion include:

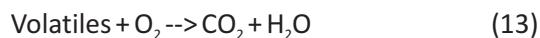
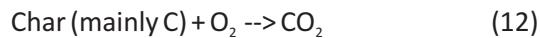
- Introduction of pure oxygen downstream of the fuel reactor, in order to oxidize the remaining unconverted gases H<sub>2</sub>, CO and CH<sub>4</sub>, so-called "oxygen polishing".
- The separation of these unconverted gases from the CO<sub>2</sub> in connection with CO<sub>2</sub> liquefaction, followed by recirculation of these gases to the fuel reactor.
- Using two fuel reactors in series, i.e. leading the incompletely converted gas from the first fuel reactor to a second fuel reactor.
- The use of a CLOU oxygen-carrier able to release oxygen in the fuel reactor

### 3.3 Chemical Looping with Oxygen Uncoupling (CLOU)

To overcome the low reactivity of char gasification stage in the iG-CLC process, an alternative option has been recently proposed. Lyngfelt and co-workers [20] made use of the idea first proposed by Lewis and Gilliland [15,21] to produce CO<sub>2</sub> from solid carbonaceous fuels by using gaseous oxygen produced by the decomposition of CuO. They discovered the importance of carriers in CLC that dissociated to produce oxygen and designated this process as Chemical-Looping with Oxygen Uncoupling (CLOU).

The CLOU process is based on the use of an oxygen-carrier which releases gaseous oxygen in the fuel-reactor thereby allowing the solid fuel to burn with gas-phase oxygen (see [Figure 3.2](#)). In this way, the slow gasification step in the iG-CLC process is avoided giving a much faster solid conversion. Likely, this process has the implication that much less oxygen-carrier material is needed in the system, which will also reduce the reactor size and associated costs. Moreover, in the direct combustion of solid fuels in the standard CLC process, the fuel-reactor must be fluidized by H<sub>2</sub>O or H<sub>2</sub>O + CO<sub>2</sub> mixtures, which also acts as gasification agents. In the CLOU process, this fluidization gas can be recycled CO<sub>2</sub>, reducing in this way the steam duty of the plant and the corresponding energy penalty.

In the CLOU process several reactions take place in the fuel reactor:



First the oxygen-carrier releases oxygen according to [reaction \(10\)](#) and the solid fuel begins devolatilization producing a porous solid (char) and a gas product (volatiles), [reaction \(11\)](#). Then, the char and volatiles are burnt as in usual combustion according to [reactions \(12\) and \(13\)](#). A scheme of this process can be seen in [Figure 3.2](#). After that the oxygen-carrier is re-oxidized in the air-reactor. For the design of CLOU systems, it is important to consider the relation among the different reactions taking place in the fuel reactor. If the oxygen-carrier decomposition rate is very rapid compared to the combustion rate of fuel, the O<sub>2</sub> concentration in the fuel-reactor will be close to equilibrium and thus the kinetics of the char combustion will determine the operating conditions on the fuel-reactor. In this case,

it is likely that specifications of CO<sub>2</sub> purity for compression and sequestration could not be fulfilled as some oxygen will be present in the gas outlet of the fuel-reactor. By contrast, if the combustion rate of fuel is faster than the oxygen release rate, the O<sub>2</sub> concentration in the fuel-reactor will be close to zero. Accordingly, the operating conditions in the fuel-reactor should maximize this release although some unburnt compounds will be present. Thus, the CLOU system must be designed having enough amount of oxygen-carrier to release the oxygen to burn the fuel, and high enough amount of solid fuel to avoid an excess of oxygen in the flue gases from the fuel-reactor. The optimum oxygen concentration in the fuel-reactor will be a compromise between the O<sub>2</sub> generation rate by the oxygen-carrier and the oxygen consumption by the fuel.

### 3.4 Oxygen Carrier fundamentals

Important criteria for oxygen-carriers are: (i) High reactivity with fuel and oxygen, and ability to convert the fuel fully to CO<sub>2</sub> and H<sub>2</sub>O, (ii) low fragmentation and attrition, as well as low tendency for agglomeration, (iii) low cost, (iv) low risk for health and environment and (v) sufficient oxygen transfer capacity.

Oxygen carrier research has focused mainly on oxides of Ni, Fe, Mn and Cu. Nickel oxide is less suitable for the solid fuels, being expensive and easily deactivated by sulfur. Iron and manganese oxides have the lowest cost and are available in the form of ores and waste materials. Copper oxide has a higher cost, but is on the other hand a CLOU material.

In addition to these monometallic oxides, metal oxides may also be combined forming new compounds with new properties. This includes Mn combined with Ca, Fe, Si, Mg, Cu and Ni [108-110] having partial CLOU properties, i.e. with the ability to release some oxygen. Moreover, a combination of Mn and Fe was found to release large quantities of oxygen rapidly [111]. With exception of calcium manganates [112, 113], these materials have not yet been tested successfully in operation. Another combined oxide is ilmenite, FeTiO<sub>3</sub>, a low-cost naturally occurring mineral often used with solid fuels.

Contrary to combined oxides, the concept of mixed oxides does not involve the creation of new compounds: Instead it builds on synergies of mixing oxygen carrier materials with different properties. An example is addition of limestone to ilmenite in solid fuel CLC [114, 115].

Studies of low-cost materials for use with solid fuels, include iron ore [116-118], manganese ore [119], ilmenite, industrial waste materials [120, 121], as well as comparisons of materials of different sources [122, 123]. Many studies have used ilmenite, e.g. [124-128], being cheap, having a reasonably high reactivity towards syngas and showing good fluidization behavior.

### 3.5 Studies on Oxygen Carriers (OCs)

The suitable materials that have the property of releasing oxygen are limited. Besides O<sub>2</sub> release, the process must be reversible as the oxygen-carrier must be oxidized again in the air reactor. Thus a special requirement is needed for the oxygen carrier to be used in the CLOU process in comparison with the oxygen-carriers for normal CLC where the fuel (gaseous or solid) reacts directly with the oxygen-carrier without any release of gas phase oxygen. Therefore, only those metal oxides that have a suitable equilibrium partial pressure of gas phase oxygen at temperatures of interest for combustion (800–1200°C) can be used as active compounds for CLOU. Three metal oxide systems have so far been identified: CuO/Cu<sub>2</sub>O, Mn<sub>2</sub>O<sub>3</sub>/Mn<sub>3</sub>O<sub>4</sub>, and Co<sub>3</sub>O<sub>4</sub>/CoO [20].

These systems can release oxygen in the gas phase through the following reversible reactions:

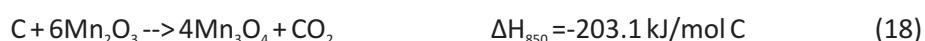


The oxygen transport capability of the oxygen-carriers, R<sub>o2</sub>, is very different depending on the reaction pairs, being 0.1, 0.03 and 0.066 for the pairs CuO/Cu<sub>2</sub>O, Mn<sub>2</sub>O<sub>3</sub>/Mn<sub>3</sub>O<sub>4</sub>, and Co<sub>3</sub>O<sub>4</sub>/CoO, respectively.

Figure 3.4 shows the partial pressure of oxygen at equilibrium conditions as a function of the temperature for these metal oxide systems. It is clear from this figure that the air- and fuel-reactor temperatures in the process must be selected based on the thermodynamic equilibrium of each metal system.

The equilibrium concentration of oxygen during carrier decomposition will be given by the temperature in the fuel-reactor, which is determined by the temperature of the incoming particles, the circulation rate in the system, as well as the heat of reaction in the fuel-reactor. A high equilibrium partial pressure of oxygen together with a very reactive oxygen-carrier will promote the overall conversion rate of the solid fuel in the fuel-reactor. In addition, the combustion of the fuel will decrease the oxygen concentration in the reactor and can improve the decomposition reaction of the metal oxide particles.

For Cu- and Mn-based oxygen-carriers, the reactions with carbon taking place in the fuel-reactor are exothermic, reactions (17) and (18). Thus, it is possible to operate at lower temperatures in the air-reactor, which results in a significantly lower partial pressure of O<sub>2</sub> at equilibrium conditions at the air-reactor exit. This fact improves the use of O<sub>2</sub> in the air stream.



On the contrary, the reaction of carbon with  $\text{Co}_3\text{O}_4$  is endothermic, reaction (19). Therefore, the temperature in the air-reactor must be higher than that in the fuel-reactor, and also higher than the one needed when Cu- or Mn-based oxygen-carriers are used.

A distinguishing characteristic of the CLOU process, relative to normal CLC, is the especially constrained operating conditions for the air-reactor due to the thermodynamic limitations of the oxygen-carrier oxidation. To maintain high power plant efficiency it is important to keep the outlet partial pressure of  $\text{O}_2$  from the air-reactor as low as possible. The oxygen concentration from the air-reactor will depend on the oxygen-carrier reactivity for oxidation reaction and the equilibrium concentration of each metal oxide system at the actual air-reactor temperature (see Figure 3.4).

Thus, the temperature in the air-reactor to oxidise the oxygen carrier should be lower for Mn- and Co-based oxygen-carriers than for Cu-based oxygen-carriers, according to Figure 3.4. This high temperature dependency of the oxygen concentration in the CLOU process makes the thermal integration between fuel-reactor and air-reactor a key aspect in the development of the technology. Table 6 shows an overview of the materials proposed in the literature as oxygen-carriers for the CLOU process. As this new option for Chemical-Looping with solid fuels was proposed recently, there is a small number of works dealing with the use of Cu [20, 129-131] and Mn-based [132-135] materials.

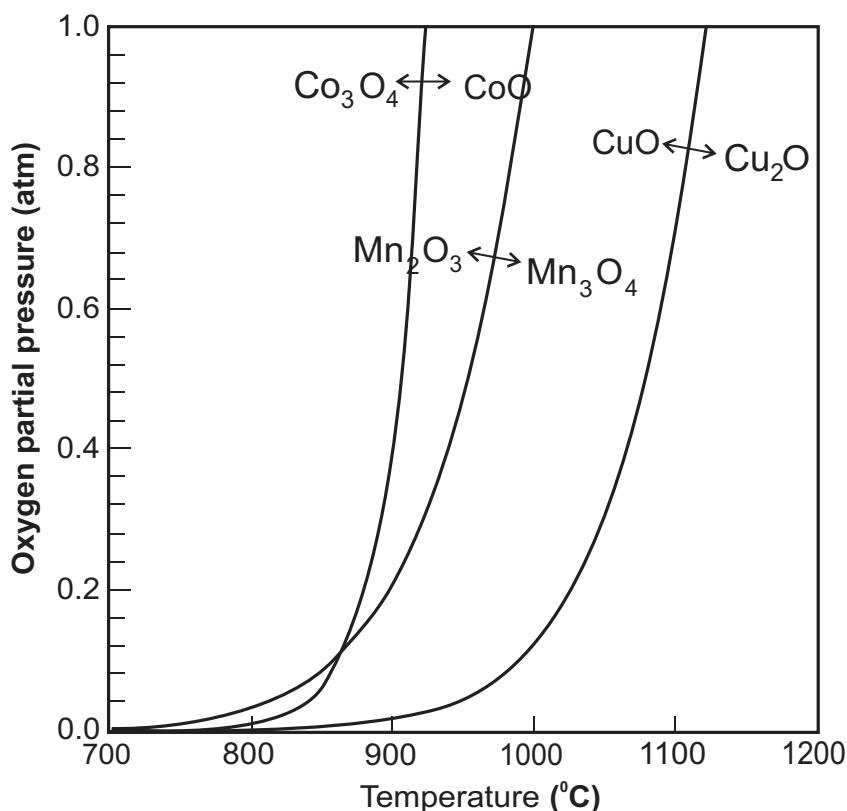


Figure 3.4 Equilibrium partial pressure of gas phase  $\text{O}_2$  over the metal oxide systems  $\text{CuO}/\text{Cu}_2\text{O}$ ,  $\text{Mn}_2\text{O}_3/\text{Mn}_3\text{O}_4$  and  $\text{Co}_3\text{O}_4/\text{CoO}$  as a function of temperature

Table - 6: Summary of the oxygen carrier particles prepared and tested for CLOU applications.

| Metal Oxide 1 (wt%)                                      | Metal Oxide 2 (wt%)                    | Support Material                 | Preparation method | Facility             | Reacting fuel                          |
|--|--|----------------------------------|--------------------|----------------------|--|
| CuO  |  |                                  |                    |                      |  |
| 60   |  | Al <sub>2</sub> O <sub>3</sub>   | FG                 | bFB                  | CH <sub>4</sub> , coke, air            |
| 40   |  | ZrO <sub>2</sub>                 | FG                 | bFB                  | Coke, coal, char, air                  |
| n.a.   |  | SiO <sub>2</sub>                 | n.a.               | TGA, bFB             | Coke, N <sub>2</sub> , air             |
| 15   |  | γ-Al <sub>2</sub> O <sub>3</sub> | IMP                | TGA                  | N <sub>2</sub> , CO <sub>2</sub> , air |
| 15   |  | MgAl <sub>2</sub> O <sub>4</sub> | IMP                | TGA                  | N <sub>2</sub> , CO <sub>2</sub> , air |
| 33   |  | γ-Al <sub>2</sub> O <sub>3</sub> | IMP                | TGA                  | N <sub>2</sub> , CO <sub>2</sub> , Air |
| 80   |  | Al <sub>2</sub> O <sub>3</sub>   | MM + PE            | TGA                  | N <sub>2</sub> , CO <sub>2</sub> , Air |
| 60   |  | Al <sub>2</sub> O <sub>3</sub>   | MM + PE            | TGA                  | N <sub>2</sub> , CO <sub>2</sub> , Air |
| 80   |  | Sepiolite                        | MM + PE            | TGA                  | N <sub>2</sub> , CO <sub>2</sub> , Air |
| 80   |  | SiO <sub>2</sub>                 | MM + PE            | TGA                  | N <sub>2</sub> , CO <sub>2</sub> , Air |
| 80   |  | TiO <sub>2</sub>                 | MM + PE            | TGA                  | N <sub>2</sub> , CO <sub>2</sub> , Air |
| 80   |  | ZrO <sub>2</sub>                 | MM + PE            | TGA                  | N <sub>2</sub> , CO <sub>2</sub> , Air |
| 60   |  | MgAl <sub>2</sub> O <sub>4</sub> | MM + PP            | TGA, bFB             | N <sub>2</sub> , CO <sub>2</sub> , Air |
| 60   |  | ZrO <sub>2</sub>                 | MM + PP            | TGA, bFB             | N <sub>2</sub> , CO <sub>2</sub> , Air |
| 40   |  | ZrO <sub>2</sub>                 | MM + PP            | TGA, bFB             | N <sub>2</sub> , CO <sub>2</sub> , Air |
| 60   |  | Sepiolite                        | MM + PP            | TGA, bFB             | N <sub>2</sub> , CO <sub>2</sub> , Air |
| 60   |  | MgO                              | MM + PP            | TGA, bFB             | N <sub>2</sub> , CO <sub>2</sub> , Air |
| 60   |  | MgAl <sub>2</sub> O <sub>4</sub> | SD                 | CLOU 1500 W          | Coal                                   |
| Mn <sub>3</sub> O <sub>4</sub>                           |  |                                  |                    |                      |  |
| 80   |  | SiO <sub>2</sub>                 | FG                 | bFB                  | CH <sub>4</sub> , air                  |
| Mixed oxides   |  |                                  |                    |                      |  |
| Mn <sub>3</sub> O <sub>4</sub> (80 - 60)                 | Fe <sub>2</sub> O <sub>3</sub> (20-40) |                                  | FG                 | bFB                  | CH <sub>4</sub> , air                  |
| Mn <sub>3</sub> O <sub>4</sub> (20-80)                   | Fe <sub>2</sub> O <sub>3</sub> (80-20) |                                  | SD                 | bFB, CLOU 300 W      | CH <sub>4</sub> , Coke, coal           |
| Mn <sub>3</sub> O <sub>4</sub> (80)                      | NiO (20)                               |                                  | FG                 | bFB                  | CH <sub>4</sub> , air                  |
| Perovskites  |  |                                  |                    |                      |  |
| CaMn <sub>0.875</sub> Ti <sub>0.125</sub> O <sub>3</sub> |  |                                  | SD + FG            | TGA, bFB, CLOU 300 W | CH <sub>4</sub> , air                  |
| Low cost materials                                       |  |                                  |                    |                      |  |
| Manganese ore  |  |                                  |                    | bFB, CLOU 300 W      | n.g.                                   |

#### 4. Developments in CLC designs

Figure 4.1 shows a scheme of the different configurations. The majority of the CLC plants existing worldwide at the moment use the configuration composed of two interconnected fluidized-bed reactors, one of them being the fuel-reactor and the other the air-reactor. In the so-called fuel-reactor conversion of the fuel happens (reaction 1), whereas the regeneration of the oxygen carrier (reaction 2) is carried out in the air-reactor. In addition, two loop-seal devices must be used in order to avoid gas leakage between reactors.

First designs using these concepts were developed for combustion of gaseous fuels at atmospheric

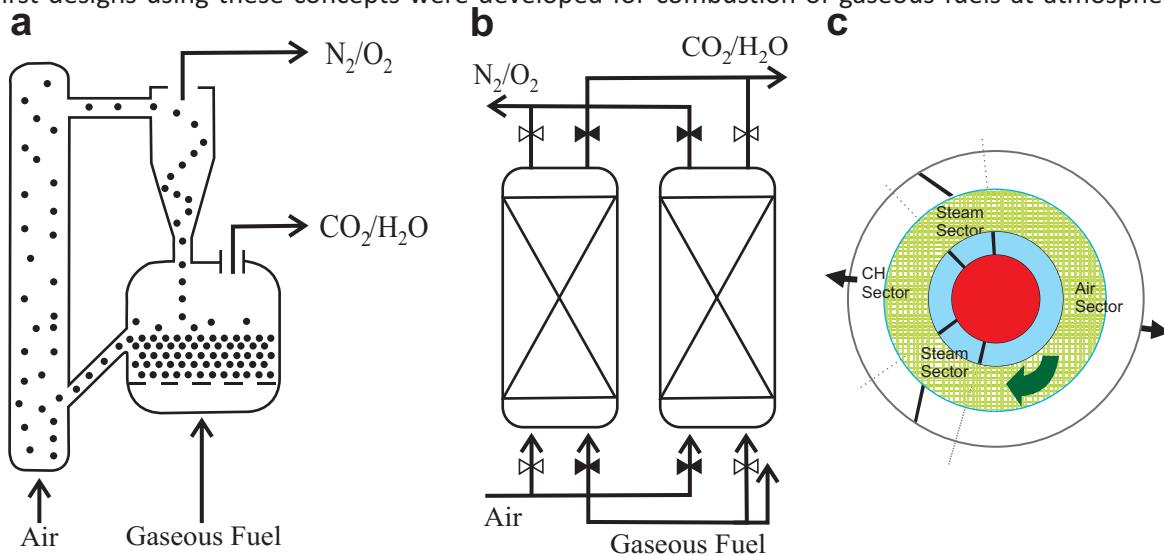


Figure 4.1 Possible reactor configurations for CLC: a) interconnected fluidized bed reactors  
b) alternating fixed bed reactors and c) rotating reactor (Hakonsem et al. [124])

pressure. Several works have been carried out to study the more appropriated design of the system. In 2001 Lyngfelt et al [137]. proposed a design based on the circulating fluidized bed (CFB) principle. This configuration has several advantages over alternative designs, considering that the process requires a good contact between gas and solids as well as a flow of solid material between the fuel-reactor and air-reactor. Other works [138-140] showed that CLC can be carried out in a variety of configurations, mainly composed of a high velocity riser and a low velocity bubbling fluidized bed as the air- and fuelreactors, respectively. The preference for this type of configuration is based on carrier reactivities [54,141] considering that most oxygen-carriers demand a higher particle residence time for the reduction reaction than for the oxidation. The riser has to fulfil two objectives: to give the driving force for the solid material circulation and shall provide sufficient oxygen to the carrier for complete fuel conversion in the fuel-reactor. Other authors have considered both reactors in the bubbling fluidized regime [55,142].

More recently, a dual circulating air-reactor and fuel-reactor directly connected by fluidization (DCFB) are used in the 120 kWth unit at TUWIEN [143]. In this system the fuel-reactor is in the turbulent regime improving in this way the gas-solid contact compared to the bubbling regime. The air-reactor is a fast bed with pneumatic transport of solids. In this configuration the solid holdup is stabilized by the direct hydraulic link between the two reactors. Moreover the solid circulation rate is only dependent on the air flow. Compared with other CLC configurations, this unit features very high solids circulation rate with low solids inventory. A different design was used by Son and Kim [144] in a 1 kWth annular shape reactor with double CFB loops for investigation into CLC. It is composed of two bubbling fluidized bed zones in the core and annular sections and two risers where the oxygen-carrier particles are circulated through each section. The annular shape of the reactor was designed to optimize heat transfer from the oxidation reactor to the reduction reactor.

Shen et al [110]. designed a 10 kWth CLC plant for biomass or coal with a spout-fluid bed instead of a bubbling bed for the fuel reactor. The spout-fluid bed has two compartments; the major compartment is called as reaction chamber, and the minor one is the inner seal. The reaction chamber allows the combination of coal gasification and oxygen-carrier reduction with coal syngas to proceed inside the spouted-fluidized bed.

In contrast with these designs, a new concept of two interconnected bubbling beds and independent solid flow control has been proposed. At IFP-France, a 10 kWth unit with three interconnected bubbling beds (one fuel-reactor and two air-reactors) and independent solid flow control has been designed and constructed. The solid circulation rates can be achieved independently of the gas flow and solids inventory in each reactor by means of pneumatic L-valves [145]. In parallel, Ryu et al [142]. developed a 50 kWth unit with control of the solids flow using solid injection nozzles inside each reactor.

In this sense, SINTEF and NTNU (Norway) have proposed a second generation 150 kWth CLC unit with focus on pressurization [146]. The unit has a double loop circulating fluidized beds operating in the fast fluidization regime. A compact design for the prospective of pressurized operation was developed in order to integrate the CLC unit into a gas turbine power cycle. However, at the moment just a full scale atmospheric cold flow version of the rig has been built and tested and solutions to improve its design have been proposed.

The more complex configuration using fluidized beds has been developed by ALSTOM for its hybrid combustion-gasification chemical looping system [24]. This system needs to operate three interactive solids transport loops (oxidizer, reducer, and sorbent calciner) at elevated temperatures, which requires advanced control systems [25]. Li and Fan [147] proposed the use of a moving bed for the CLC process. Due to its solid plug flow, the use of this reactor configuration is based on the theoretical higher solid conversion in a moving bed than in a fluidized bed, reducing in this way the needed reactor volume. However, results from their coal direct Chemical-Looping process tested in a 2.5 kWth moving bed unit at Ohio State University using an iron-based oxygen carrier are still missing. More recently, Schwebel et al [148]. had also suggested the use of a new reactor concept for implementing CLC using a parallel arrangement of a moving-bed fuel-reactor and a fluidized-bed airreactor, especially for solid fuels. The authors claimed that this configuration avoids fuel segregation together with a less char at the reactor exit and less power demand for fluidization. However, this approach has a restricted thermal power per unit approximately of 20 MWth.

With respect to power cycle burning gaseous fuels, to achieve competitive energy efficiencies it is necessary to operate at high temperatures and high pressures (1-3 MPa) [149,150]. In this sense, operating pressurised CLC plants using interconnected fluidized bed technology could have some technical difficulties to maintain a stable solid circulation between the reactors. With the aim to work under pressure, dynamically operated packed-bed reactors have been proposed [151,152]. At least two reactors in parallel working alternately must be used to assure a continuous high temperature gas stream supply to the downstream gas turbine. The process consists of alternate oxidation and reduction cycles in two separate reactors, intermittently alternated with short periods of mild fluidization of the bed after each cycle to level off temperature and concentration profiles. The main advantages of packed-bed reactor technology are that the separation of gas and particles is intrinsically avoided and the possibility to work under pressure. Disadvantages of the concept include the necessity to use a high temperature, high flow gas switching system. A full scale powerplant using this technology would need a sophisticated system of valves for different feeds and outlet gases that might be a problem and also the pulsed operation for the gas turbines. Moreover the heat transfer in a packed bed must be carefully analysed, being this characteristic very important for the process. A first evaluation of the concept was made with a Cu-based oxygen-carrier and CH<sub>4</sub> as fuel [151, 152]. However higher temperature differences and deeper radial temperature profiles can be expected working with oxygencarriers based

on nickel or iron in CH<sub>4</sub> combustion.

Dennis et al [153, 92]. have proposed the use of a cycling fedbatch operation for solid fuels in order to reduce the attrition problems associated with the conveying of large quantities of solids in the interconnected fluidized beds configuration. In this operation mode, three consecutive periods of time (fuel feeding, char combustion without fuel feed, and oxygen-carrier regeneration with air) are carried out in only one fluidized reactor. However, for industrial practice, several reactors at different stages would be needed in order to load the power cycle. This scheme has just been experienced at lab-scale.

Finally, a rotating reactor was proposed by Dahl et al [154,136]. In this reactor, the oxygen-carrier material is rotated between different gas streams flowing radially outwards through the metal oxide bed. Between the two reacting streams one inert gas is introduced to avoid mixing of the two reacting gases. The main challenge in this reactor concept is to avoid gas mixing between fuel and air streams, which at the moment are unavoidable.

Operational experiences from twelve CLC units, most of them using gaseous fuels, have previously been reviewed[155]. Below data from nine solid fuel CLCs are presented, [Table 7](#). Chalmers' 10 kW CLC combustor has been used in several studies using different solid fuels with ilmenite and manganese ore. Gas conversion was poor in the earlier studies, but significantly improved with a redesign providing in-bed feeding of the fuel, to 77% for coal and around 80% for petcoke [156]. Manganese ore was found to give significantly improved gas conversion, around 87% for petcoke, and a dramatic increase in the rate of steam gasification of char, [\[156\]](#). Gas conversion was also improved by addition of limestone.

A 10 kW unit in Nanjing has been operated with coal and biomass using nickel- and iron-based oxygen carriers. Further work with iron ore has been done in a smaller 1 kW solid fuel unit in Nanjing. The ratio of carbon containing gases from the FR was typically 1% CH<sub>4</sub>, 4% CO and 95% CO<sub>2</sub>.

At CSIC a 0.5 kW solid fuel unit was used in comprehensive studies of the effect of operating conditions using coal and ilmenite. Gas conversion was in the range 70–95% with coal, and close to 100% using char. Furthermore, the unit demonstrated the first successful operation of CLOU with 100% gas conversion [\[157\]](#). At IFP a 10 kW pilot with three reactors, i.e. two air reactors in series, was operated with coal and a natural ore,[\[158\]](#). Gas conversion was around 90%.

At Hamburg University of Technology, an Australian ilmenite was operated with lignite dust in a 25 kW unit,[\[159\]](#). The fuel reactor was a two-stage reactor, and CO<sub>2</sub> concentrations above 90% were reached in the gas from the fuel reactor. Two units of 2.5 and 25 kW using moving beds with supported iron oxides were operated with coals and other solid fuels at Ohio State University. CO<sub>2</sub> concentrations above 99% were reported, [\[160\]](#). A 100 kW solid fuel unit at Chalmers was operated with bituminous coal and

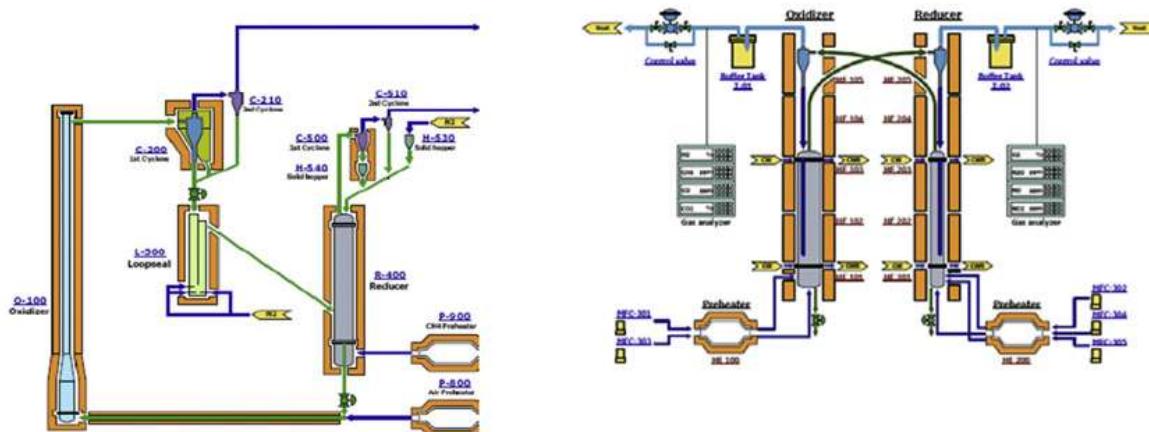
ilmenite, Figure 4.2. With bituminous coal gas conversions up to 84% were reported, and the CO<sub>2</sub> capture was around to 98%[161]. Gas conversion increased with bed mass in fuel reactor, as well as with reduced volatiles content.

Furthermore two bigger solid-fuel chemical-looping pilots have been erected, a 1MW<sub>th</sub> unit at University of Darmstadt and a 3MW<sub>th</sub> unit at Alstom Power Plant Laboratories. Testing has started in both and initial results look promising [162, 163].

Totally, more than 1000 h of solid fuel operation in nine units of sizes 0.5–100 kW, using different oxygen-carriers and fuels has been reported. This demonstrates both that the process works, and that there are suitable oxygen-carriers for this new combustion technology.

Table-7: Operational experiences in solid fuel chemical looping combustion

| Location | Size (kW) | Oxides tested                                 | Time (hr) | Fuel          | Year |
|----------|-----------|---|-----------|---------------|------|
| Chalmers | 10        | Ilmenite, Mn Ore                              | 90        | Coal, Petcoke | 2008 |
| Nanjing  | 10        | NiO, Fe <sub>2</sub> O <sub>3</sub>           | 230       | Coal, Biomass | 2009 |
| Nanjing  | 1         | Fe <sub>2</sub> O <sub>3</sub>                | >20       | Coal, Biomass | 2010 |
| CSIC     | 0.5       | Ilmenite, CuO, Fe <sub>2</sub> O <sub>3</sub> | 164       | Coal          | 2011 |
| IFP      | 10        | Natural ore                                   | 52        | Coal          | 2012 |
| Hamburg  | 25        | Ilmenite                                      | 21        | Coal          | 2012 |
| Ohio     | 2.5       | Fe <sub>2</sub> O <sub>3</sub>                | 300       | Solid fuels   | 2012 |
| Ohio     | 25        | Fe <sub>2</sub> O <sub>3</sub>                | 230       | Coal          | 2012 |
| Chalmers | 100       | Ilmenite                                      | 23        | Coal          | 2012 |



50 kW<sub>th</sub> KIER-1 CLC for gaseous fuels KIER, Korea    50 kW<sub>th</sub> KIER-2 CLC for gaseous fuels KIER, Korea

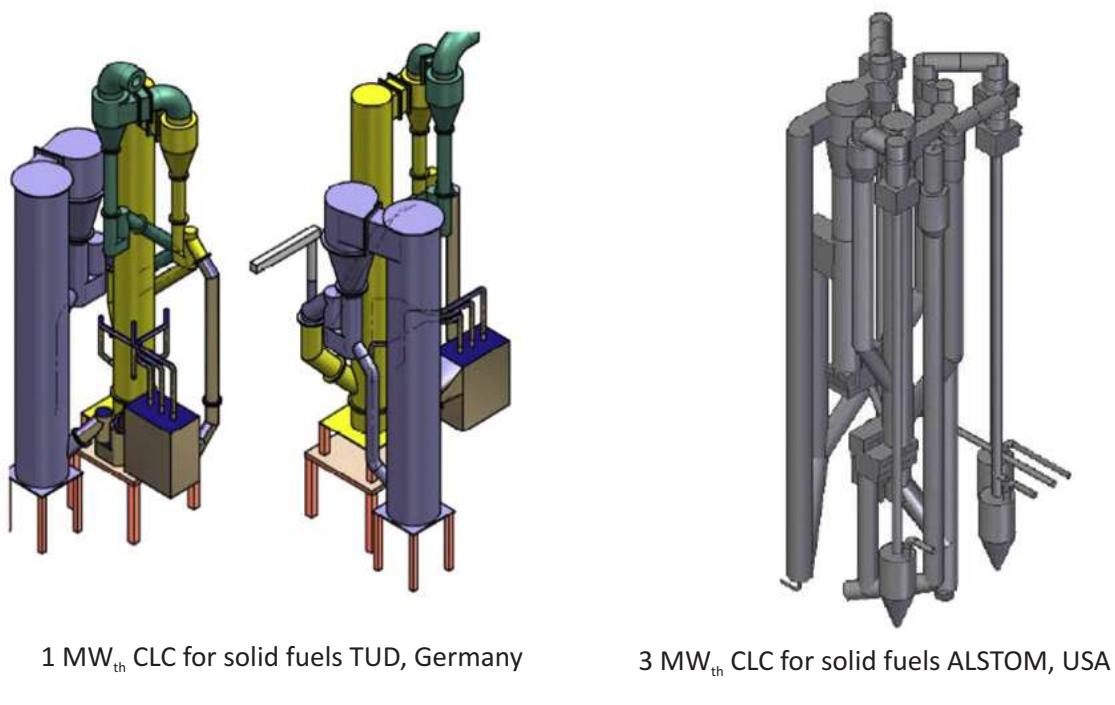


Figure 4.2. Some of the CLC systems installed for gaseous and solid fuels

## 5. Modelling Studies on CLC

The modelling of the fuel- and air-reactors is helpful for the design, optimization, and scale-up of the CLC process. An interesting number of works can be found in the literature for the modelling of the reactors involved in a CLC system, as is presented in [Table 9](#). Most of them are developed for the two interconnected fluidized-bed reactors concept. As commented in [Section 2.1.1.](#), this is the most used configuration for a CLC system. The air-reactor is designed as a high-velocity riser and the fuel-reactor as low velocity bubbling fluidized bed. Nevertheless, the fuel-reactor can be operated in the fast fluidization regime, where the gas velocity is higher than in the bubbling regime, to increase the fuel load [164].

Modelling of fluidized-bed reactors can be divided into three main fields, which are closely connected: fluid dynamics, reaction scheme and kinetics, and heat balance. Fluid dynamics describe the kind of contact between reacting gases and solids. The reaction scheme must consider the relevant reactions happening in the reactor taking into account the kinetics of every reaction. Finally, the heat balance is necessary to know the distribution temperature in the reactors and the heat flux that must be extracted from the reactors. Fluid dynamics, mass balances and heat balances in the reactor must be solved simultaneously because of the variation of reaction rates and gas properties. Thus, the actual reaction rate in every position inside the reactor, the appearance of side-reactions, the possible gas expansion as fuel is converted (e.g. when methane or coal is used), the growth of the bubble size, or relevance of reactions in the freeboard are other factors to be considered.

The mathematical modelling of each reactor will improve the understanding of the fluid dynamics coupled with the complex chemistry happening in the reactors. In addition, the solids circulation flow rate and the solids inventory in the CLC reactors can be evaluated.

## 5.1 Reaction kinetics

The solids inventory in the fuel- and air-reactors predicted by models is linked and depends on the reactivity of the materials and on the oxygen transport capacity of the oxygen-carrier [140, 54]. To account for the reaction rate of gases and solids, the kinetic of the reactions is included in the model according to the reaction mechanism proposed.

An intensive work has been done in the past about the reactivity and kinetic determination of the reduction and oxidation of metal oxides supported or un-supported for metallurgical applications and catalyst characterization [165]. However, the application of the experience achieved for metallurgical applications cannot be directly applied to the reactions involved in the CLC process for several reasons, namely: (i) the oxidized and reduced compounds cannot be the same as that for CLC, especially for Fe [63] and Mn based oxygen-carriers; (ii) the analysis of the reduction or oxidation was limited to the use of fresh or pre-treated particles, but in a CLC system the solid particles suffer repeated reduction and oxidation cycles, which can affect their chemical and physical properties; and (iii) the experimental condition e.g. temperature, particle size, gas composition are usually different than those required for CLC. Thus, the reaction kinetics for the oxidation and reduction should be determined for oxygen-carriers at typical conditions in a CLC system.

To adequately design the CLC reactors, the knowledge of the reaction kinetics of the solid oxygen-carrier with the reducing gases and oxygen in air are required. The kinetics for all the reactions involved in the reaction scheme must be determined. For example, if H<sub>2</sub> and CO were intermediate products during CH<sub>4</sub> conversion, reaction kinetic for reduction with H<sub>2</sub> and CO must be considered. Reactivity data for a huge number of materials have been reported in the literature, but usually they are obtained for one single operational condition [31]. Limited information can be extracted for design purposes from the reactivity data, although they can be used for comparison purposes among different oxygen-carriers. It must be considered that the oxygen-carrier will be found in different environments during their stage in the fuel- and air-reactors. Thus, it is necessary to determine the reaction rate under different operating conditions of temperature and gas concentration. The reactions involved in the fuel- and air-reactors with the oxygen-carrier can be considered as non-catalytic gas-solid reactions.

Different models for gas-solid reactions have been used to predict the time dependence of the conversion of oxygen-carrier particles and the effect of operating conditions on the reaction rate. The most frequently used models are the Changing Grain Size Model (CGSM), the Shrinking Core Model (SCM), and nucleation and nuclei growth models [166].

## 5.2 CFD studies

Fluid dynamics of the reactor must depict both the flow and distribution of gaseous compounds and solid particles in the reactors. It is well known that restrictions for the gas-solids contact e.g. the

resistance to gas diffusion between bubble and emulsion phases in the dense bed are relevant in a fluidized bed. For CLC, experimental results obtained in lab-scale fluidized-bed reactors have been adequately predicted by models neglecting these physical processes [106]. But it is likely that these assumptions will not be fulfilled for CLC systems at higher scale because of the use of highly reactive oxygen-carriers and the high velocity of gas related to most gas flowing through the bubbles. The predicted solids inventories to fully convert the fuel gas to CO<sub>2</sub> and H<sub>2</sub>O considering diffusional resistances have been found to be between 2 and 10 times higher than those found when these effects were neglected [167]. These results reveal the importance of considering the mechanisms limiting the gas-solids contact in the fluidized-bed reactors. Based on the description of the fluid dynamics of the reactor, mainly two categories of models can be differentiated, as it is shown in [Table 8](#): macroscopic fluid dynamics models, and computational fluid dynamics models (CFD). These models consider the complex gas flow and solids distribution in the reactors involved in a CLC system.

The macroscopic models consider the distribution of the gas flow among emulsion and bubbles as well as the distribution of solids concentration in the bed by using empirical equations. The more complete models also include the solids distribution in the freeboard region above the dense bed, see [Table 8](#). An attempt to consider the diffusion resistance between bubbles and emulsion was done by Kolbitsch et al [168], by using a model parameter,  $f_s$ , core, which simulates an effective amount of solids exposed to gas phase. This simple model describes the behaviour of both the fuel and air-reactors and how the conversion of solids is coupled by the reaction in these reactors. However, it is difficult to know the actual value of this parameter in a fluidized bed, which could be different in different zones of the reactor.

Models based on the two-phase theory for bubbling fluidized beds [169] or for fluidized beds in the turbulent or fast fluidization regime [170] have been used for CLC simulation. These models were developed to predict the fluid dynamics of large fluidized bed reactors. Actually, the vertical profile of solids predicted by the model described by Pallarés and Johnsson [170] showed good agreement with the experimental data for units as large as 226 MW circulating fluidized beds (CFB) and adequately predicted the combustion efficiency burning biomass in a 12 MW<sub>th</sub> CFB boiler [171]. Thus, the macroscopic models have a great potential to be used for the simulation, design and optimization of large fluidized bed reactors in CLC systems. These models integrate the complex chemistry where a fuel gas, e.g. natural gas, reacts with a continuously circulated oxygen-carrier, with the complex fluid dynamics of large fluidized-bed reactors, using low computing time (order of minutes). In this way, modelling and simulation of the fuel-reactor for CH<sub>4</sub> as fuel gas has been developed for a 10 kW<sub>th</sub> bubbling fluidized bed and a 120 kW<sub>th</sub> high-velocity fluidized bed [167,172].

These models have been validated against experimental results obtained in the CLC units built at ICB-CSIC and TUWIEN, respectively. The computational fluid dynamic codes (CFD) are based on the first

principles of momentum, heat and mass transfer and do not require detailed assumptions in the modelling procedure. These models can simulate the behaviour of the reactor during a transient time until the steady-state is reached. To date few CFD simulations have been performed of a full CFB due to the complexities in geometry and the flow physics, requiring a large computational effort (order of several hours). The task of simulating a full scale CFB is very challenging, and improvement of CFD methods for modelling full scale fluidized beds is in development [173]. However, with the improvement of numerical methods and more advanced hardware technology, the use of CFD codes is becoming more affordable. CFD models for commercial scale bubbling fluidized bed has been recently presented [174,175]. Therefore, the use of CFD models can be of interest for the development of the CLC technology in the near future.

The fluid dynamics for the full loop, i.e. air-reactor, cyclone and fuel-reactor, in a small scale cold-flow model has been successfully modelled by using CFD codes [176-178]. [Figure 5.1](#) shows the solids distribution in the system predicted by the CFD model in the whole loop [178]. However, limited works have been carried out using CFD codes to simulate a CLC system. CFD models are being developed for bubbling fluidized beds, being very sensitive to the bursting of bubbles at the top of the bed and the fluctuations in the concentration of gas at the reactor exit are predicted [179-181]. However, these models either do not consider the solids fraction in the freeboard, or it is under-predicted because of the low conversion of gas predicted in this zone by CFD models. Notice that gas solids reaction in freeboard has been revealed of high importance to predict the high fuel conversion experimentally observed [167].

Most of CFD models have been developed for reactors in batch mode, without solids circulation, or for small scale CLC systems ( $300\text{-}1000\text{ W}_{\text{th}}$ ). Important progress has been done validating the CFD models with experimental results obtained in small-scale facilities using gaseous fuels [182-184], or coal [185]. Up to date, the more complete modelling of a CLC system using CFD codes is the simulation of a bubbling fluidized bed for the fuel-reactor coupled to a riser for the air-reactor using methane as fuel and Mn- or Ni-based oxygen-carriers [186, 187].

The relatively complex processes affecting the reaction of fuel gas with the oxygen-carrier such as full fluid dynamics, reactivity of the oxygen-carrier, the reaction pathway and the effect of solids circulation rate has not yet been modelled using CFD codes in the range of the status of the CLC technology ( $10\text{-}150\text{ kW}_{\text{th}}$ ). Until CFD codes for CLC process are more accessible and robust, the macroscopic models are effective tools for the simulation, design and optimization of CFB technologies.

Summary of theoretical models for CLC

| Reference              | Oxygen-Carrier and Fuel      | Reactor Model <sup>a</sup>   | Solid distribution <sup>a</sup>   | Reactor Size <sup>b</sup>                    |
|------------------------|------------------------------|--|---|--|
| Macroscopic Models     | Kolbitsch et al [336]        | OC: 60wt% NiO on $\text{Al}_2\text{O}_3$ Fuel: $\text{CH}_4$<br>OC: 60 wt% CuO on $\text{SiO}_2$ Fuel: $\text{CH}_4$<br>OC: 60wt% NiO on $\text{Al}_2\text{O}_3$ Fuel: $\text{CH}_4$<br>OC: 60 wt% NiO on YSZ Fuel: $\text{H}_2$ | FR&AR: Dense bed: single-phase Freeboard: exponential decay<br>FR: Bubbling fluidized bed Dense bed: two phases Freeboard: exponential decay<br>FR: Bubbling fluidized bed Dense bed: two phases Freeboard: exponential decay<br>FR: Bubbling fluidized bed Fast fluidization regime Dense Bed: two phases AR:<br>Riser: core-annulus | HCD<br>RTD<br>PB<br>PB                       |
|                        | Adámez et al. [337, 338]     |  | FR: Bubbling fluidized bed Dense bed: two phases Freeboard: exponential decay   | 120 kW <sub>th</sub><br>6.5 MW <sub>th</sub> |
|                        | Kronberger et al. [339]      |  | FR: Bubbling fluidized bed Dense bed: two phases Freeboard: exponential decay   | 10kW <sub>th</sub>                           |
|                        | Xu et al. [340]              |  | FR: Bubbling fluidized bed Dense bed: two phases Freeboard: exponential decay   | 45 kW <sub>th</sub>                          |
|                        |                              |  | Riser: core-annulus   |  |
| CFD Models             | Abad et al. [200]            | OC: 14 wt% CuO on $\text{Al}_2\text{O}_3$ Fuel: $\text{CH}_4$  | FR: Bubbling fluidized bed Dense bed: two phases Freeboard: exponential decay   | RTD<br>RTD                                   |
|                        | Abad et al. [341]            | OC: 40 wt% NiO on $\text{NiAl}_2\text{O}_4$ Fuel: $\text{CH}_4$  | FR: Fast fluidization regime Dense bed: two phases Freeboard: core-annulus  | HCD<br>Batch mode (v)                        |
|                        | Iliuta et al [164]           | OC: 15 wt% NiO on $\text{Al}_2\text{O}_3$ Fuel: $\text{CH}_4$  | FR: Bubbling fluidized bed Dense bed: three phases Freeboard: no  | HCD<br>Batch mode (v)                        |
|                        | Borwn et al. [119]           | OC: $\text{Fe}_2\text{O}_3$ Fuel: Char   | FR: Bubbling fluidized bed Dense bed: two phases Freeboard: no  | HCD<br>1 MW                                  |
|                        | Ströhle et al. [334]         | OC: Ilmenite Fuel: Coal  | FR: Fast fluidization regime Dense bed: PSR Freeboard: PSR  | HCD<br>Batch mode                            |
|                        | Pavone et al. [342, 343]     | OC: Ni coated monolith Fuel: $\text{CH}_4$   | Alternating step Flow through channels  | -<br>Continuous operation                    |
|                        | Noorman et al. [116, 117]    | OC: Ni coated monolith Fuel $\text{CH}_4$  | Rotating reactor Flow through channels  | -<br>Batch mode (v)                          |
|                        | Deng et al. [344, 345]       | OC: CuO on $\text{Al}_2\text{O}_3$ Fuel: $\text{CH}_4$   | Alternating step Packed Bed   | -<br>Batch mode                              |
|                        | Jin et al. [346]             | OC: $\text{CaSO}_4$ Fuel: $\text{H}_2$   | Alternating step Packed Bed   | -<br>Batch mode                              |
|                        | Jung and Gamwo [347]         | OC: 58 wt% NiO on bentonite Fuel $\text{CH}_4$   | FR: Bubbling fluidized bed Freeboard: no  | HCD<br>Batch mode                            |
| and Shuai et al. [348] | Cloete et al. [349]          | OC: 58 wt% NiO on bentonite Fuel: $\text{CH}_4$  | FR: Bubbling fluidized bed Freeboard: no AR: Riser  | HCD  |
|                        | Krugge-Emden et al. [350]    | OC: 40 wt% $\text{Mn}_3\text{O}_4$ on $\text{Mg-ZrO}_2$ Fuel: $\text{CH}_4$  | FR: Bubbling fluidized bed Freeboard: no AR: Riser  | HCD  |
|                        | Mahalalkar et al. [351]      | OC: 40 wt% $\text{Mn}_3\text{O}_4$ on $\text{Mg-ZrO}_2$ Fuel: $\text{CH}_4$  | FR: Bubbling fluidized bed Freeboard: no  | HCD<br>0.3 kW <sub>th</sub> (v)              |
|                        | Mahalalkar et al. [352, 353] | OC: Fe-Ni on bentonite Fuel: $\text{CH}_4$   | FR: Bubbling fluidized bed Freeboard: no  | HCD<br>1 kW <sub>th</sub> (v)                |
|                        | Mahalalkar et al. [354]      | OC: 60 wt% $\text{Fe}_2\text{O}_3$ on $\text{MgAl}_2\text{O}_4$ Fuel: Coal   | FR: Bubbling fluidized bed Freeboard: no  | HCD<br>batch mode (v)                        |

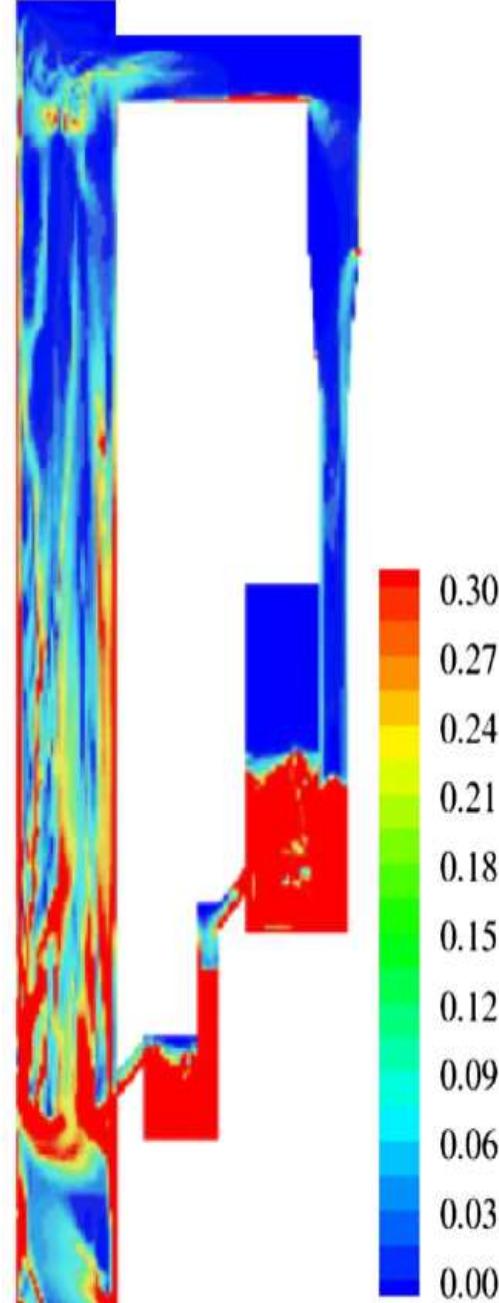
<sup>a</sup> AR: air-reactor; FR: fuel-reactor; CFD: computing fluid dynamic; PSR: perfectly stirred reactor; RTD: residence time distribution; PB: population balance; HCD: homogenous conversion distribution.

Figure 5.1 Predictions of solids distribution by CFD model in two interconnected fluidized beds, as proposed for CLC [178]

### 5.3 RTD studies

The appropriate distribution of solids residence time in the reactor must be considered in the reactor model. The particle residence time distribution (RTD) in the reactor influences the reaction rate of solids in the reactor. Thus, very different conversion of gas were obtained using different distribution functions for the solids conversion, even though they may have the same average conversion [188]. Three different approximations have been proposed to consider the distribution of solids conversion in the reactor: (1) homogeneous conversion of solid particles in the reactor, which has been used mainly in CFD models; (2) a population balance to the solid particles [188,189]; and (3) a residence time distribution of solids in the reactor [53,167,172]. Usually, it is considered that the solids are in perfect mixing inside fluidized-bed reactors, which has shown to be true for mixing among solids in the dense bed and the freeboard zone [139]. Exceptionally at low fluidizing velocities,  $u_g/umf < 10-15$ , this assumption cannot be maintained because the appearance of stagnant zones [139]. At these conditions the use of a homogeneous conversion in the reactor could drive to unsuitable results.

The average reaction rate of the particles having a RTD function  $E(t)$  in the fuel- or air-reactor can be calculated by

$$\bar{-r_o} = R_{OC} \int_0^{\tau} \frac{c}{dt} dX_s E(t) dt \quad (18)$$

The average reactivity has been expressed to consider that the oxygen-carrier is introduced into the fuel- and air-reactor partially converted, with a mean conversion  $X_{s,in}$ . The variation of solids conversion proceeds from  $X_s = 0$  at  $t = 0$  to  $X_s = 1 - X_{s,in}$  at  $t = T_c$  [40,178]. Abad et al [53] introduced the characteristic reactivity of the reactor,  $\Phi_j$ , to calculate the average reaction rate from the known rate of oxygen transfer at  $X_s = 0$ ,  $(-r_o)$ .

## 6. Outlook for Development

### 6.1 Future Research and prospects

CLC has possible applications in the oil and gas industry to replace conventional CO<sub>2</sub> capture systems in heaters and boilers. For example, refinery gas and fuel oil are used at the moment to deliver their internal energy requirements. In the case of CLC using refinery gas as fuel, the selection of the solid material could be determined by the effect of minor compounds present in the fuel, i.e. sulfur and light hydrocarbons, on the oxygen-carrier behaviour.

In addition, the oil industry is showing great interest in the use of liquid fuels, such as heavy hydrocarbons, in a CLC system for heat and steam generation. Possible applications can be found in a refinery complex or in the in-situ extraction of heavy oil seams. However, limited studies with oxygen-carriers to process liquid fuels are present in the open literature.

Regarding the intensive use of coal for energy generation, there is an increasing interest in the use of CLC for solid fuels. In fact, this is the more relevant application field of CLC technology at this moment. Direct combustion of coal in the CLC process is investigated to avoid the oxygen needed in coal gasification for further CLC syngas combustion. In situ gasification of coal in the fuel reactor using cheap oxygen-carriers as natural minerals or industrial waste products is very promising. This technology needs to improve combustion efficiency in order to reduce the intensity of an oxygen polishing step, and to optimize the carbon stripper design to maximise the CO<sub>2</sub> capture efficiency. The use of the CLOU process for solid fuel combustion using oxygen-carriers that can release oxygen at high temperature is another promising alternative.

This process facilitates the implementation of the technology because the carbon stripper is avoided. Relevant advances in this technology are now under way, especially in the development of materials with CLOU properties. Regarding H<sub>2</sub> production by Chemical-Looping technologies, a-CLR has been demonstrated at scales up to 140 kW avoiding the need of oxygen in the process. The economy of this technology will be highly improved if pressurised reactors are used. The steam reforming integrated with Chemical-Looping Combustion (SR-CLC) has an important potential although needs to be demonstrated at higher scale.

A cornerstone in the successful development of all the CLC technologies is the oxygen-carrier material. It must be considered that cost of the oxygen-carrier is the main added cost of this technology. An economic balance should consider the cost of the raw materials, the cost of particle preparation, the oxygen-carrier lifetime, disposal and environmental costs. Therefore, it is important to have a portfolio of oxygen-carriers, both synthetic and low cost materials, with specific characteristics adequate for different fuels (coal, natural gas, refinery gas, syngas, liquid fuels, etc.) and Chemical-Looping processes (CLC, CLR).

CLC technology has suffered a great advance in different aspects such as material development and process design. Until now, CLC/a-CLR has been demonstrated at scales up to 120-140 kWth with natural gas and the operation of 1 MW<sub>th</sub> & 3 MW<sub>th</sub> CLC plant with coal is currently underway. The scale up of the technology is a very important issue that needs to be accomplished. Demonstration of the CLC process with different fuels at demo scale and an examination of the impact of high temperatures on materials and engineering components need further consideration. This would result in a more reliable and safer operation. In addition, a life cycle assessment and the environmental impact of the Chemical-Looping technologies are aspects to be analyzed.

At the moment, most of the know-how is based on operation at atmospheric pressure. However, higher energetic efficiency is obtained with pressurized operation by means of the use of combined cycles for electricity generation. This is especially important for the use of gaseous fuels in power industry because

of the competition with gas turbine combined cycle plants with conventional CO<sub>2</sub> capture. Therefore, CLC and CLR under pressure is an important challenge for natural gas combustion and reforming. Key elements will be the development of control systems for solid circulation between interconnected fluidized beds.

## 6.2 Key Conclusions and the way forward

Chemical-Looping Combustion (CLC) has emerged during last few years as a very promising technology for power production and industrial applications with CO<sub>2</sub> capture. The advantages of these technologies come from their inherent CO<sub>2</sub> capture mechanism which avoids the energy penalty in this process when compared with other competing technologies.

Most of the experience has been gained for the use of gaseous fuels with long term tests (up to 1000 h) and operation in continuous plants up to 3000 MW<sub>th</sub>. An important benchmark has been reached in the development of the oxygen-carriers, through testing of more than 700 different materials mainly based on nickel, copper and iron. The total time of operational experience in continuous units including all fuels and technologies is about 3500 h at the end of 2012.

An additional advantage with CLC is that the gas coming out of the air reactor can be expected to be essentially free from harmful emissions such as NO<sub>x</sub> and SO<sub>2</sub>. Compounds formed from nitrogen and sulfur in the fuel will be concentrated in the smaller gas stream from the fuel reactor, which should facilitate separation.

Although more development work is needed, especially with respect to finding the best design of the fuel reactor system, it is clear that the CLC technology provides a unique potential for avoiding the large costs and energy penalties inherent in gas separation.

The following conclusions can be made:

- The technology is similar to established combustion of coal in circulating fluidized bed.
- There is a unique potential for dramatic reduction in cost and energy penalty for CO<sub>2</sub> capture.
- CLC operation with low-cost mineral such as ilmenite works well, but to reach high performance additional development is needed, either with regards to reactor system or the oxygen carrier material used.
- Oxygen carrier materials other than ilmenite could provide significant improvement of performance, but it is not clear if they are available at reasonable costs.
- The following options to have a complete conversion of the gas to CO<sub>2</sub>/H<sub>2</sub>O in the fuel reactor are available:

- (i) oxygen polishing,
- (ii) separation/recycling of unconverted gas,
- (iii) using two fuel reactors in series and
- (iv) CLOU oxygen carriers

For scale-up, a more detailed understanding of the processes in the fuel reactor is needed to design and optimize the fuel reactor system, in order to assess how the performance will be affected by the properties of the oxygen carrier and the reactor design.

The optimization of the fuel reactor system will primarily need to consider three costs, i.e. costs for oxygen carrier, costs for the fuel reactor system, and costs downstream of the fuel reactor to accommodate for incomplete conversion, e.g. oxygen polishing. Consequently, a good understanding of these costs is needed to find the optimal solution, and realize the great potential of this technology.

Given that a price must be paid to implement CO<sub>2</sub> capture from fossil fuel power plants, CLC seems to be an economical alternative in comparison to other proposed approaches. As a consequence, the future of the Chemical-Looping technologies will be very promising during the next years and commercial scale implementation will certainly occur in the medium term.

This work reveals the potential of CLC integration in power plant, especially for the countries having large coal reserves and also those recently adopting IGCC technologies. This study is more valuable for the countries like India where the major thermal power production is from coal. This technology can also be considered as an option for the retrofitting of existing power plants to reduce their carbon foot print.

## Abbreviations

AR - Air-Reactor

ASU - Air Separation Unit

a-CLR - Autothermal Chemical-Looping Reforming

CACHET - Carbon Dioxide Capture and Hydrogen Production from Gaseous Fuels

CCCC - Capture of CO<sub>2</sub> in Coal Combustion

CCP - CO<sub>2</sub> Capture Project

CCS - CO<sub>2</sub> Capture and Storage

CDCL - Coal Direct Chemical Looping

CFB - Circulating Fluidized Bed

CFC - Chlorofluorocarbon

CFD - Computing Fluid Dynamics

CGSM - Changing Grain Size Model

CHALMERS - Chalmers University of Technology

CLC - Chemical-Looping Combustion

CLCCC - CLC-Combined Cycle

CLCs - Solid fuelled Chemical-Looping Combustion

CLCp - Pressurized Chemical-Looping Combustion

CLH - Chemical-Looping Hydrogen

CLOU - Chemical-Looping with Oxygen Uncoupling

CLR - Chemical-Looping Reforming

COP - Coprecipitation

DCFB - Dual Circulating Fluidized Bed

DR-CLCCC, Double reheat CLC-combined cycle

DRM - Diffusion-Reaction

FR - Fuel-Reactor

GHG - Greenhouse Gas

GWP - Global Warming Potential

ICLC-CC - Integrated Chemical-Looping Combustion Combined Cycle

iG-CLC - In-situ Gasification Chemical-Looping Combustion

IGCC - Integrated Gasification Combined Cycle

IPCC - Intergovernmental Panel on Climate Change

MEA, Methyl Ethanolamine

OC - Oxygen-Carrier

OSD - One Step Decarbonization

RTD - Residence Time Distribution

SCL - Syngas Chemical Looping

SCM - Shrinking Core Model

SEM - Scanning Electron Microscope;

SR - Steam Reforming

SR-CLC - Steam Reforming integrated with Chemical-Looping Combustion

SR-CLCCC - Single reheat CLC combined cycle

TGA - Thermogravimetric Analyzer

TITECH - Tokyo Institute of Technology

TPO - Temperature Programmed Oxidation;

TPR - Temperature Programmed Reduction

TUD - Darmstadt University of Technology

TUWIEN - Vienna University of Technology

UNFCCC - United Nations Framework Convention on Climate Change

WGS - Water Gas Shift

XRD - X-ray Diffraction

YSZ - Yttria Stabilized Zirconia.

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