



Evolution, Fields of Research, and Future of Chemical-Looping Combustion (CLC) process: A Review

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ABSTRACT

This study presents a review on Chemical looping combustion (CLC) development, design aspects and modeling. The CLC is in fact an unmixed combustion based on the transfer of oxygen to the fuel by a solid oxygen carrier material avoiding the direct contact between air and fuel. The CLC process is considered as a very promising combustion technology for power plants and chemical industries due to its inherent capability of CO₂ capturing, which avoids extra separation costs of the CO₂ from the rest of flue gases. This review covers the issues related to oxygen carrier materials. The modeling works are reviewed and different aspects of modeling are considered, as well. The main drawbacks and future research and prospects are remarked.

Keywords: Chemical looping combustion (CLC), CO₂ capture, Gas-solid reaction kinetics, Oxygen carrier

1. Introduction

The global warming effect is leading to life threatening problems for human and other living creatures all around the world. This effect may be a consequence of the increasing greenhouse gases emissions into the earth's atmosphere due to the human activities. The CO₂ in specific as the most significant greenhouse gas accumulates in the earth's upper atmosphere and enhances the greenhouse effect and global warming. Nearly all the developing and developed countries use fossil fuels to supply their energy requirements. The CO₂ concentration in the atmosphere has increased strongly over the few past decades as a result of world dependency on fossil fuels for energy production [1-3] and global atmospheric concentration of CO₂ increased from a value of 280 ppm to 390 ppm [1, 2, 4]. The CO₂ concentration should be kept at 450 ppm to ensure that global temperatures do not rise by more than 2 °C (which is considered as a limit to prevent abrupt changes in earth) [1]. Therefore, there is an urgent demand to develop technologies for reduction of emissions of this gas. CO₂ capture and storage (CCS) is an appropriate option to reach this objective. The purpose of CCS technologies is to produce a concentrated stream of CO₂ from industrial sources, transport it to a suitable storage location and then store it away from the atmosphere for a long period of time [1, 3, 5, 6].

So far, mainly three technologies for CO₂ capture are under consideration for industrial and power plants applications: pre-

combustion, oxy-fuel combustion and post combustion. All of these methods are energy-intensive and lead to considerable plant low efficiency. Pre-combustion CO₂ capture is a process where the carbon in the fuel is separated, or removed, before combustion process. Instead of burning coal or natural gas in a combustion plant, the fuel can be converted to hydrogen and CO₂ prior to combustion. The CO₂ can then be captured and stored, while the hydrogen is combusted to produce power. Oxy-fuel process needs pure oxygen for burning the fuel; consequently demands for energy to separate oxygen from the air. Post combustion needs energy to remove the CO₂ diluted with other gases in the power plant exhaust stream. Great efforts are made in the recent years to develop new low-cost CCS technologies. Chemical looping combustion (CLC) is an appropriate alternative to reduce economic cost of CO₂ capture from combustion of fossil fuels in power plants [1-4]. Chemical-Looping term is used for cycling processes that use a solid metal oxide as oxygen-carrier for supplying the required oxygen for fuel conversion. The fuel reduces the solid metal oxide. To complete the loop, the solid metal oxide must be re-oxidized before to a new cycle begins. The final purpose of fuel conversion can be the combustion or hydrogen production. For combustion purposes, the chemical looping process takes place in two steps, while air and fuel are kept away from each other in two separate reactors referred to as air and fuel reactors. Here, the combustion air (oxygen) and fuel direct contact is avoided. Therefore, the CLC can be called as unmixed combustion process. The first step,



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in fuel reactor, the oxygen supplied to fuel by the oxygen carrier, where the fuel reduces the metal oxide by taking up the required oxygen. In the second step, this reduced metal oxide re-circulates into the air reactor where it is re-oxidized by air. Since, the air and fuel are not in direct contact, the combustion gases are not diluted with N_2 , consequently separation of CO_2 is not required [1-3, 7-9]. This avoids extra separation cost of CO_2 from flue gases. CLC process uses gaseous or solid materials as fuels. In CLC of gaseous fuels, the oxygen carrier reacts directly with a fuel such as natural gas, refinery gas, etc. However, there are different possibilities for processing solid fuels like coal and biomass including: Syngas-CLC, in-situ Gasification CLC (iG-CLC) and chemical looping with oxygen uncoupling (CLOU) [1, 6]. A short description of these processes is presented here. In the Syngas-CLC process, the solid fuel is gasified in a gasifier to form a syngas and then the oxygen carrier come into contact with this syngas in the air reactor. Although the fuel fed to CLC is gaseous, the primary fuel is in solid state. In iG-CLC process the gasification and combustion can occur in a unique reactor. The oxygen carrier reacts with gasification products of solid fuel generated inside fuel reactor. The CLOU method is basically different from the two previous ones. CLOU uses the oxygen carriers which are able to release gaseous oxygen for the combustion of solid fuel [1, 6].

In this review, the important challenges related to CLC process with respect to experimental and modeling studies, especially on gaseous fuels are presented. This article covers the main recent findings on CLC process through available experimental and theoretical studies as follows in section 2, a short review on process development is presented. Section 3 covers the status of the development of oxygen carrier materials and discusses main achievements in this field. The reactor design aspects are discussed in section 4. Advances on mathematical modeling of CLC process and the main progresses in this field are presented in section 5. The most important kinetic models are mentioned in this section, as well. Section 6 includes the drawbacks and future prospects of CLC process.

2. Process Overview of Chemical Looping Combustion

Lewis and Gilliland [10] introduced CLC concept for the first time in a patent entitled "production of pure carbon dioxide" in 1954. They introduced the concept of oxygen carrier, with the possibility to use different fuels to reduce it and the use of two interconnected fluidized bed for the solid circulation. The principles of CLC process to increase thermal efficiency in fossil fuel power plants is proposed in the early eighties [1, 9]. Ishida, et al. [11] introduced the name of chemical looping combustion in their study to reduce exergy loss caused by the conversion of fuel energy to thermal energy in conventional power plants using natural gas. Ishida and Jin [12] developed CLC as a process to capture CO_2 using Fe- and Ni- based oxygen carriers.

In a CLC-based power plant the outlet gas stream of air reactor drives gas (air) turbine while the exhaust gas from the fuel reactor derives a CO_2 turbine. The exhaust from the air turbine is circulated

through a heat recovery steam generator to produce steam, which is used in the low pressure steam turbine to generate extra power. After circulating through the CO_2 turbine, the exhaust gas from the fuel reactor, is further cooled to nearly ambient temperature in order to condense the water, leaving almost pure CO_2 (greater than 90%). Finally, the concentrated CO_2 stream is compressed for transportation and sequestration [1].

Anheden and Svedberg [13] performed a detailed energy analysis for two different CLC gas turbine systems. In the first one, methane was used as fuel and NiO as oxygen carrier, while in the second system; the used fuel was gasified coal (CO and H_2) and Fe_2O_3 was used as oxygen carrier. The power efficiency in both cases was 48%, which is comparable to the one of a conventional power generation station. However, taking into account the advantages of inherent CO_2 separation, a CLC-based process offers higher overall energy efficiency.

The application of CLC process at larger scales is the next step in developing of this technology. Lyngfelt, et al. [14] introduced the first basic design concepts of an atmospheric circulating fluidized bed (CFB) boiler with a power of 10 MW_{th}.

There is an increasing interest in developing CLC technology because of the advantages described before. Investigations on this process are being conducted in many countries such as Sweden, Japan, Korea, Spain, Norway, Italy and the United States [15].

The CLC processes have about 3,500 hours of operational experience in continuous plants of different size. Considering that the experimental experience of this process is less than 10 years old, it is assumed that the process development status is very successful [1].

3. Oxygen Carriers

The large scale application of CLC process greatly depends on the availability of suitable oxygen carriers [2, 16]. The selection of oxygen carrier is considered as one of the most essential issues of the process [2, 16, 17]. In fact the amount of the bed material in each reactor and solid circulation rates between reactors mainly depend on oxygen carrying capacity of oxygen carrier material. The most important features of suitable oxygen carrier can be listed as follows:

- High reactivity in both the reduction and oxidation cycles
- Ability to convert the fuel and achieve to maximum fuel combustion efficiency in a complete manner
- Good stability under repeated oxidation/reduction cycles at high temperatures
- Appropriate fluidization properties (good resistance to agglomeration)
- Negligible carbon deposition that would release CO_2 in the air reactor reducing the CO_2 capture efficiency
- Enough mechanical resistance against stress associated with high circulation of particles
- Being environmentally benign and economically feasible [12, 16-19].

A number of metal oxides are investigated as potential oxygen carriers for CLC process. In general, it is considered that transition metal oxides like nickel, copper, cobalt and manganese are among the feasible candidates to be used as an oxygen carriers [1, 2,

16, 18, 20-22]. Initially the bulk metal is investigated as the oxygen carrier. Good reactivity is observed in the first several cycles. Although bulk materials have low cost, their fast degeneration and low reactivity (mainly due to the particle agglomeration and changes of crystalline form of these materials) make them unsuitable for application in CLC process. To overcome these drawbacks, an inert material can be added into the oxygen carries [22]. These inert materials act as a supports which can provide a vast specific area and appropriate pore structure for reaction. These inert support can act as a binder for increasing the mechanical strength and attrition resistance, as well [16, 22, 23]. These materials enhance the reactivity, durability and fluidizability of the oxygen carrier particles [2, 16]. The active metal oxides can be applied on different inert materials such as Al_2O_3 , MgAl_2O_4 , SiO_2 , TiO_2 , ZrO_2 , bentonite, sepiolite, etc. [16, 20-22]. One of the important features of an oxygen carrier is oxygen transport (carrying) capacity also called oxygen ratio which is defined by the following Eq. (1).

$$R_o = \frac{m_{ox} - m_{red}}{m_{ox}} \quad (1)$$

where, m_{ox} and m_{red} are the masses of oxygen carrier in fully oxidized and fully reduced form, respectively [17, 22, 23]. The maximum values of RO are reported for the NiO and CuO, and this value is low for the Fe_2O_3 in its transformation onto Fe_3O_4 . Different oxygen carriers may be reduced to different states depending on the metal dispersed on the support materials. For example, iron compounds have different oxidation states (Fe_2O_3 - Fe_3O_4 - FeO - Fe). It should be noted that, only the transformation from hematite to magnetite may be applicable for industrial CLC systems [23].

Obviously, the inert support decreases the oxygen transport capacity of the oxygen carriers [22, 23]. Different proportions of active metal oxide and inert support can yield different kinds of oxygen carriers [22]. The oxygen carrying capacity depends on both the active metal oxide content (x_{MeO}) and the type of the metal oxide [23].

Normally, the support material is considered to be inert with respect to any phase in the reaction. However, the experimental findings reveal that the inert support would react with the active carrier to form a complex chemical compound. For example in NiO/ Al_2O_3 oxygen carrier, the undesirable formation of NiAl_2O_4 is reported after a reduction in the fuel reactor [22]. Therefore, the oxygen carrier capacity is corrected by active metal content factor (x_{MeO}) in oxygen carrier, as Eq. (2).

$$R_{o,OC} = R_o x_{MeO} \quad (2)$$

The oxygen transport capacity of some oxygen carriers has been reported in (Table 1). In order to select a suitable oxygen carrier, the thermodynamic aspects and physical properties like particle size, density, active surface area, pore volume, crushing strength, anti-agglomeration properties and melting point must be considered [2, 22]. Some researchers reported a thermodynamic criterion for selection of an oxygen carrier in possible CLC operating temperatures (600–1,200°C). They presented the equilibrium constant

Table 1. The Oxygen Transport Capacity of Conventional Oxygen Carries [22]

Metal oxide	Inert support	Mass ratio of MeO (%)	Oxygen transport capacity	Complex compound
NiO	Al_2O_3	20-60	0.043-0.16	NiAl_2O_4
	NiAl_2O_4	40-60	0.09-0.13	-
	MgAl_2O_4	37-60	0.09-0.13	NiAl_2O_4
	TiO_2	40-60	0.09-0.13	NiTiO_3
	SiO_2	41	0.083	-
CuO	Al_2O_3	14-35	0.027-0.08	CuAl_2O_4
	MgAl_2O_4	43	0.087	CuAl_2O_4
	SiO_2	39	0.012	-
Fe_2O_3	Al_2O_3	60	0.027	FeAl_2O_4
	MgAl_2O_4	32	0.0096	FeAl_2O_4
Mn_2O_3	SiO_2	47	0.048	-
Mn_2O_3	MgAl_2O_4	46	0.047	-
Mn_2O_3	Al_2O_3	28-60	0.02-0.07	-
Mn_2O_3	MgZrO_2	40	0.028	-

K (logarithmic scale) versus $1/T$ plots for reduction of some common materials using methane as the reducing agent (fuel), with a high log K value indicating high metal oxide potential to react with methane. According to these studies, $\text{MnO}_2/\text{Mn}_2\text{O}_3$, $\text{Mn}_2\text{O}_3/\text{Mn}_3\text{O}_4$, $\text{Co}_3\text{O}_4/\text{CoO}$ and $\text{CuO}/\text{Cu}_2\text{O}$ have greater tendency to react with methane compared to $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ and NiO/Ni. However, MnO_2 , Mn_2O_3 , Co_3O_4 , and CuO decompose into Mn_2O_3 , Mn_3O_4 , CoO and Cu_2O , respectively, at low temperatures. Thus, these materials may not be suitable oxygen carriers. In addition, the results of this analysis indicate that the $\text{Mn}_2\text{O}_3/\text{Mn}_3\text{O}_4$, $\text{CuO}/\text{Cu}_2\text{O}$, $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ and NiO/Ni carriers are able to convert methane to CO_2 almost completely [2].

Johansson, et al. [18] compared fifty oxygen carrier materials in CLC process of methane. The carries were based on Fe, Mn and Ni oxides which had different metal oxide/inert ratio, sintering temperature and type of inert. They reported that, in general, nickel particles are the most reactive, followed by manganese. The Fe particles are hard with low reactivity. An increase in sintering temperature raises the particle strength while leading to a decrease in oxygen carrier reactivity.

3.1. Ni Based Oxygen Carriers

The Ni based oxygen carriers can be used at high temperature 900-1,100°C range in a CLC process with full conversion of methane although thermodynamic limitations cause the generation of small amount of CO and H_2 in the fuel reactor outlet [1, 16]. Usually pure NiO has a poor performance which is the result of nickel agglomeration. This affects its reactivity and makes it unsuitable for CLC [2]. So it can be assumed that the use of an inert material is suitable. YSZ (Yttria-Stabilized Zirconia) is one of the support materials for synthesis of Ni based oxygen carriers. It has a major contribution to an increase in the oxidation rate of NiO [16]. Based on the available literature particles with YSZ support presented good reactivity and regenerability [1, 2, 16]. However, the price

of YSZ is higher in comparison with other inerts [16]. Among available support material alumina has received the highest ranking because of its favorable fluidization properties and thermal stability [1, 2, 16]. Furthermore, it is much cheaper than YSZ [16]. The formation of NiAl_2O_4 is an unfavorable issue in this type of oxygen carriers [1, 2, 16, 22]. Once this complex is formed a good fraction of the nickel remains without contributing to the fuel combustion cycle [2]. To overcome this drawback, NiO based oxygen carriers can be prepared with modified Al_2O_3 via thermal treatment or chemical deactivation with Mg or Ca oxides. The NiAl_2O_4 can be used as a support instead of Al_2O_3 [1, 2, 16, 22]. The NiO/ NiAl_2O_4 is considered as one of the most promising oxygen carriers for CLC due to its good reactivity and high thermal ability above 900°C [16]. Other inert materials like SiO_2 , TiO_2 , bentonite and zirconia are also studied as support for NiO based oxygen carries [1, 2, 16]. The reactivity of both the NiO/ SiO_2 and NiO/ ZrO_2 materials decrease after repeated reduction-oxidation cycles above 900°C due to formation of unfavorable nickel complexes. Despite some of mentioned drawbacks nickel oxides supported on alumina are promising potential oxygen carrier materials for large scale CLC applications [2].

3.2. Cu Based Oxygen Carriers

The Cu based oxygen carriers have the highest oxygen transport capacity allowing system operation with lower solid flow rates between the two reactors. Furthermore, when CuO is used as oxygen carrier, the oxidation and reduction reactions in air and fuel reactors are exothermic which eliminates the need of energy supply in fuel reactor. Cu based carriers are highly reactive in both the reduction and oxidation reactions and the reduction reaction can reach complete conversion using gaseous fuels like methane [1, 2, 16]. Despite these advantages, the CuO has not received significant attention specially due to its tendency to become decomposed at low temperatures, its low melting point and its tendency to agglomeration [2]. Based on some findings, CuO/ Al_2O_3 carriers with a CuO content of lower than 10 wt% never agglomerated in the fluidized bed but when the active metal content becomes more than 20 wt% agglomeration is inevitable [16].

The SiO_2 is studied as a support material by a number of researchers. This findings indicate that SiO_2 is quiet inert to Cu even at high temperature and there is no tendency to complex formation between support and active metal oxide [2]. Findings of some studies on performance of CuO/ SiO_2 in chemical looping of methane in a fixed bed reactor reveal that after 20 cycle neither performance decay nor mechanical degradation of oxygen carrier is observed [16]. The TiO_2 and ZrO_2 are used as inert material for Cu based oxygen carriers. TiO_2 has specific restrictions to be used in CLC due to the tendency of copper to form CuTiO_4 [2].

3.3. Fe Based Oxygen Carriers

Iron based materials are low cost and environmentally friendly, making them attractive to be used in CLC process despite their weak characteristics like low methane conversion and oxygen transport capacity [1, 2, 16]. Fe based materials have different oxidation states when Fe_2O_3 is reduced but due to thermodynamic considerations only the transformation of Fe_2O_3 into Fe_3O_4 is applicable in CLC systems based on interconnected fluidized bed [1, 16].

The Fe based materials have enough reactivity at both the atmospheric and pressurized conditions especially for H_2 and CO. This reactivity is lower for methane [2]. Fe_2O_3 based oxygen carriers are prepared on different supports like Al_2O_3 , ZrO_2 , TiO_2 and MgAl_2O_4 [2, 16]. Some researchers suggest that $\text{Fe}_2\text{O}_3/\text{MgAl}_2\text{O}_4$ have the best reactivity among the iron oxides supported on other mentioned inert materials [16]. It is found that by using TiO_2 the available oxygen of Fe_2O_3 is reduced due to the formation of FeTiO_3 . Similar results are observed for $\text{Fe}_2\text{O}_3/\text{SiO}_2$ due to formation of Fe_2SiO_4 [2, 16].

Natural iron ores, like hematite and ilmenite, are used as oxygen carriers, especially for solid fuels. Ilmenite leads to a high conversion of CO and moderate conversion of CH_4 [1, 16]. Mattisson, et al. [8] used natural hematite in CLC of methane at 950°C in a fixed bed reactor. It is found that the majority of methane converted into CO_2 with some small formation of CO during reduction period. They reported that there is some breakage of particles due to chemical reactions.

3.4. Mn Based Oxygen Carriers

There are few studies on Mn oxides as oxygen carrier in CLC process [1, 16]. The use of pure Mn oxides show low reactivity with methane or coal [1]. Al_2O_3 , Sepiolite, SiO_2 and TiO_2 are unsuitable inert materials for Mn oxides, while ZrO_2 is the best inert material [1, 16]. Particles prepare with ZrO_2 have good reactivity and stability through repeated oxidation-reduction cycles but they experience a phase transformation which produces cracks in their structure. These particles display agglomeration, as well [1]. To overcome these drawbacks, Mn based oxygen carriers are synthesized with ZrO_2 stabilized by addition of MgO, CaO or CeO_2 . These materials display high reactivity and insignificant physical changes during the reaction cycles [1, 16].

Mattisson, et al. [24] studied the performance of some metal oxides supported on alumina including $\text{Mn}_3\text{O}_4/\text{Al}_2\text{O}_3$. It is found that this material displays poor reactivity mostly due to formation of MnAl_2O_4 which does not react with the fuels.

3.5. CaSO_4 Oxygen Carriers

Recently some researchers conducted studies on the feasibility of using CaSO_4 as oxygen carrier in CLC process [1, 16, 17, 25]. CaSO_4 has the maximum oxygen transport capacity among the carriers tabulated in Table 1. Moreover, it is a low cost material [16, 17, 22]. This material is reduced to CaS in fuel reactor in CLC process of gaseous fuels [1, 17, 25].

The CLC process of CH_4 with CaSO_4 are studied by some researchers in a fixed bed where they found that CaSO_4 has good reactivity and thermal stability [16]. The main drawback for the use of CaSO_4 is the formation of CaO through side reactions which evolve SO_2 to the reaction products. The SO_2 formation becomes higher at high temperatures [1, 16]. Generation of CaO in fuel or air reactor leads to a decrease in CaSO_4 oxygen transport capacity; hence it is necessary to add fresh particles into the system. To minimize the SO_2 formation it is found that the air reactor temperature should be within $1,050\text{-}1,150^\circ\text{C}$ range and fuel reactor should work at temperature within $900\text{-}950^\circ\text{C}$ range [1]. It is found that adding a low amount of fresh limestone into the CLC system

can capture SO_2 and the products of CaSO_4 and CaS can be used as oxygen carriers later [16].

3.6. Mixed Oxygen Carriers

Each one of the single oxygen carriers has its own advantages and disadvantages. It is claimed that, combined metal oxides may sometimes provide a better properties than single metal oxides [1, 2, 16, 22]. Therefore in recent years the mixed oxygen carrier materials are becoming the focus of some studies on oxygen carrier material development [1, 2, 16, 22, 26-28].

Hossain and de Lasa [29] prepared a bimetallic $\text{Co-NiAl}_2\text{O}_3$ oxygen carrier for a fluidized bed CLC process. According to these researchers, the mentioned oxygen carrier displays excellent reactivity and stability. Using Co minimizes the formation of NiAl_2O_4 and inhibits particle agglomeration during the redox cycles. Also mixed metal oxides of CoO-NiO/YSZ display a good reactivity and significant regenerability for repeated cycles of reduction and oxidation than single related metal oxides [2, 16, 22]. Despite this good properties, the CoO-NiO/YSZ oxygen carrier has not received further attention and this may be due to the low thermal stability and high cost of YSZ support [2]. Mixed oxygen carriers of Ni-Fe base materials is also studied by different researchers [26, 27]. It is found that adding NiO to $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ particles improves the activity but decreases the mechanical strength [1]. Son and Kim [30] carried out some experiments in a CFB using different Fe-Ni /bentonite ratios. Based on attrition tests and cost, the optimum ratio of $\text{NiO/Fe}_2\text{O}_3$ is 3. According to these researchers, there is a direct relation between the reactivity of oxygen carrier and NiO content increase.

Siriwardane, et al. [28] acquired an oxygen carrier with optimized CuO and Fe_2O_3 composition to achieve high reactivity and great stability. They reported that the oxygen carriers with more than 40% CuO , less than 45% Fe_2O_3 and less than 30% inert material like Al_2O_3 displays the best performance. Two oxygen carriers with composition of $60\text{Cu}20\text{Fe}20\text{Al}$ and $40\text{Cu}40\text{Fe}20\text{Al}$ have the highest reaction rates and fuel conversion while minimizing agglomeration. All bimetallic $\text{CuO-Fe}_2\text{O}_3$ oxygen carriers displayed better physical stability in comparison with pure CuO .

3.7. Oxygen Carrier Synthesis

The physical properties are important features to choice a proper oxygen carrier. Since the CLC process is usually operated between 600 and 1,200°C, there is a concern about some metals when the selected operating temperature is close to their melting point. For example, Cd , Zn and Ce with melting points below or close to 600°C, are unsuitable for CLC systems. Cu has a relatively low melting point (1,085°C), as a consequence, cannot be used above 900°C.

Other important physical properties are the density and particle size. These properties not only determine the fluidizability of the oxygen carrier but also affect the overall reaction rate due to their effect on mass and heat transfer inside the particles [2]. The oxygen carriers with particle sizes ranging from 0.08 to 2 mm [2, 22] and density within 1.5 to 4.5 kg/m^3 are suitable for CLC [22]. The crushing strength of the particles is another important property due to the physical stresses associated with fluidization. The crushing strength for most of the available oxygen carriers is within of 3.7-5.2 N range [2, 22].

The preparation method of oxygen carrier material determines the physical properties such as the particle size, shape, density, mechanical strength and porosity in a direct manner which can influence the reactivity. So far, the synthesis methods reported in the related literature includes mechanical mixing, impregnation, dispersion, frozen granulation, Sol-Gel methods and spray drying process.

Frozen granulation and impregnation methods are usually used in oxygen carrier synthesis because their operation is easier than that of the other mentioned methods. The former is frequently used for synthesis of Ni and Fe based materials while the latter is used for Cu based oxygen carriers. The proper porosity and specific surface area is observed through these two methods. The sol-gel method can produce finer and well-distributed particles; however the process is difficult and costly. The shape of oxygen carrier produced by mechanical mixing is irregular while other methods produce particles with a better degree of sphericity.

The sintering process fixes the active phase onto the inert support. The sintering temperature and time will affect the property of the prepared materials. It is revealed that the higher temperature and longer time can increase the mechanical strength but reduce the reactivity. Therefore, the proper temperature and time should be determined. The selection of appropriate additives such as starch and graphite can also improve the porosity of the inert or the mixture of oxygen carries [22].

Generally speaking, the reactivities of the four supported oxygen carrier are in the descending order of NiO , CuO , Mn_2O_3 and Fe_2O_3 , respectively, while this order depends on how the oxide is supported [16]. Cu , Ni , Co and their oxides display higher oxidation and reduction reactivities and greater durability after repeated oxidation and reduction cycles compared to Fe -based oxygen carries [21]. It should be noted that most reactive particles are the most expensive ones [15]. Furthermore, they often involve safety and health issues, meaning that regardless of low reactivity, iron based materials are low cost and environmentally friendly [21]. The mixed metal oxides can be used to combine the advantages of each sole oxides and to some extent improve their properties [16].

Based on the discussed issues on oxygen carriers, here it is worthwhile to pay attention to some points. There are a great number of materials which can be used as supporting materials for oxygen carrier synthesis. The ratio of active and supporting material can be very versatile and there are many possible procedures to produce oxygen carrier materials. Furthermore, in each method there are some parameters which can determine the final product properties. The oxygen carrier quality is significantly affected by physical properties and purity of source materials. Thus, it is not possible to fix an optimal condition to all applications, science the optimal properties vary depending on the application and should be adjusted based process as a whole. These issues reveal that one of the most important challenges in developing a CLC process is selection or synthesis of a proper oxygen carrier which would meet all process requirements.

4. CLC Process Design Aspects

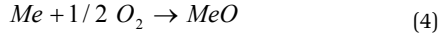
The CLC is a tow-step combustion process. A solid oxygen carrier (OC) circulates between two reactors and transports oxygen from

the combustion air to fuel. Since the fuel is not mixed with air, the flue gas from fuel reactor is not diluted with N_2 and the subsequent CO_2 separation is not necessary [5, 9, 22]. A simple schematic of a CLC process is shown in Fig. 1.

The gaseous fuel reduces the oxygen carrier in fuel reactor by following overall equation (Eq. (3)):



The oxygen carrier re-oxidized in air reactor through the Eq. (4):



The reduction of oxygen carrier by methane is an endothermic reaction for the most of oxygen carrier materials, except of CuO , while the oxidation reaction is always exothermic. Obviously, it is an advantage of using CuO , since it reduces the number of solid circulation which is needed to set and control the temperature of fuel reactor [15]. However, the low melting point of copper is its drawback. An exothermic reaction is typical in air and fuel reactors for all oxygen carrier materials if H_2 and CO is used as a fuel. Regardless fuel or oxygen carrier used in the process, the net heat of a CLC process is the same of the heat of conventional combustion of fuel [5, 8, 9, 15, 22] because when the reduction reaction is endothermic, the oxidation reaction has a higher heat of reaction than conventional combustion of the fuel gas [1].

The CLC process is studied in different reactor configurations such as alternating fixed and packed beds [31-33], rotating reactors [34] and interconnected fluidized beds. Since the process requires a good contact between gas and solid as well as a flow of solid material between two reactors, it is found that the use of two interconnected fluidized beds have advantages over other reactor configurations [1, 2, 8, 9, 16, 23]. The volumetric gas flow in the air reactor is larger than that of fuel reactor. To maintain a reasonable size of the reactors a high velocity riser is adopted for air reactor while the fuel reactor is a bubbly fluidized bed reactor. The high velocity in the riser (air reactor) provides the required driving force to circulate the particles between the two

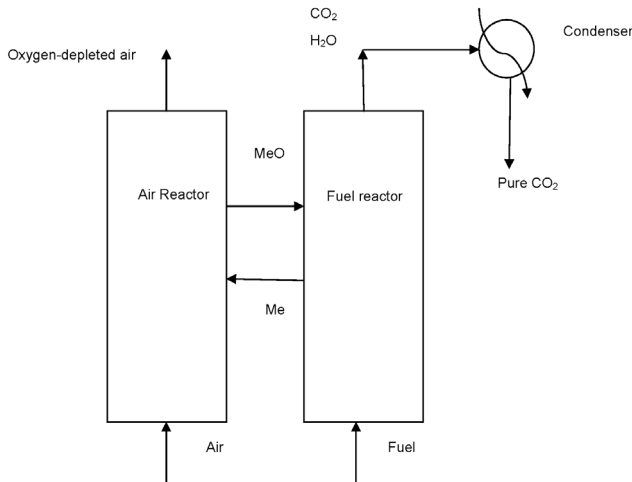


Fig. 1. Schematic of chemical-looping combustion (CLC) process.

interconnected beds. The particles carried away from the riser are recovered by a cyclone and fed to the fuel reactor. The particles from the fuel reactor are returned to the air reactor by gravity [1, 2, 23].

The dual circulating fluidized bed is another reactor configuration which is used for CLC process. In this system the fuel reactor is in the turbulent regime to improve gas-solid contact compared to the bubbling regime. The air reactor is fast bed with pneumatic transport of solids. The significant solid circulation rate and low solid inventory (amount of bed materials) are the features of this configuration [1].

The majority of CLC studies are conducted at atmospheric pressure, so the use of interconnected fluidized beds is more useful than the other configurations. However, in power cycle burning gaseous fuels, to achieve competitive energy efficiencies it is necessary to operate at high temperature and pressures (1-3 MPa). In pressurized CLC it is difficult to maintain a stable solid circulation between two reactors. To overcome this issue, dynamically operated packed-bed reactors are proposed [1, 17]. In this configuration, at least two parallel reactors 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 [1]. It is found that during the oxidation cycle an air stream with constant and very high temperature can be generated [31]. The main advantage of packed-bed reactor technology is that the separation of gas and particles is intrinsically avoided [1, 17, 31] and there is no need to design a cyclone for separating the solid particles from gas stream. This particle separation is particularly difficult at high temperature and pressures. This problem becomes more important considering the fact that even fines produced by particle attrition must be removed to protect the downstream gas turbine [31].

The necessity of using a high temperature, high flow gas switching system, is the disadvantage of the packed bed configuration. A full scale power plant using this technology would need a complicated system of valves for different feeds and outlet gases that might be a problem. This also creates a pulsed operation mode for the gas turbines. Moreover, the use of packed beds lowers the degree of mixing in reactors and can lead to formation of undesirable hot spots in them [17], and hence the temperature control in packed beds is another problem which is very important issue in CLC process [1, 17].

The design of a CLC system is predominantly determined by the properties of the oxygen carrier and fuel gas type. For a CLC system based on two interconnected fluidized beds the circulation rate of solids between two reactors must be high enough to transfer the adequate oxygen for the fuel combustion and the heat necessary to maintain the heat balance in the system, if necessary. As noted, the most important property of an oxygen carrier is its oxygen transport capacity or oxygen ratio which is defined by Eq. (1). In fact, oxygen ratio is the mass fraction of oxygen in the carrier at its fully oxidized state.

For a 1 MW_{th} of fuel and assuming its full conversion, solid circulation rate can be obtained by Eq. (5).

$$\dot{m}_{Oc} = \frac{b_r M_{MeO}}{x_{MeO} \Delta x_s \Delta H_c^0} = \frac{dM_{O_2}}{R_{O,OC} \Delta x_s \Delta H_c^0} \quad (5)$$

where, b_r is the stoichiometric coefficient of fuel in reduction reaction, d is stoichiometric coefficient for O_2 in the conventional combustion reaction of fuel, M_{O_2} , M_{MeO} are the molecular weight of oxygen and oxygen carrier respectively. The ΔH_c^0 is the standard combustion heat of the fuel and Δx_s is the difference in solids conversion between the inlet and the outlet of the fuel or air reactors.

The conversion of solid material in oxidation reaction is given by Eq. (6):

$$x_s = \frac{m_{ox} - m}{m_{ox} - m_{red}} \quad (6)$$

where, m is the instantaneous mass of oxygen carrier material.

The circulation rate in a CFB system depends on operating conditions and the riser configuration [1, 23]. Based on the available literature, the superficial gas velocity in air and fuel reactors can be determined, respectively based on the particle size used and the regimes of fluidization to be maintained in the reactors. These values are used to calculate the area of each reactor. For typical condition of gas velocity (4-6 m/sec), temperature (850-950°C) and excess air (0%-20%) a value of 0.2 m²/MW can be selected as an average riser area considering the combustion of CH₄, CO and H₂. Based on this average area (S) the solid flow can be calculated by Eq. (7):

$$G_s = \frac{\dot{m}_{OC}}{S} \quad (7)$$

The Fe-based oxygen carriers because of their low oxygen transport capacity (Table 1) need much higher circulation rates compared to the Ni- and Cu-based oxygen carriers. The values from 20 to 100 kg/m²sec are reported for G_s in literatures [23].

5. Modeling of CLC Process

The modeling of fuel and air reactors is helpful for design, optimization and scale-up of a CLC process [1]. Most of the works in related literature are developed for two interconnected fluidized bed reactor. It is the most used configuration in CLC process design. Modeling of a fluidized bed reactor can be divided into three main fields including fluid dynamics, reaction scheme and kinetics, which are closely related to each other [1, 7]. The models developed in literature can be included in the two general groups: macroscopic models based on empirical correlations for fluid dynamic of a fluidized bed and multiphase computational fluid dynamic (CFD) models.

5.1. Macroscopic Models

The macroscopic models are generally based on the two-phase theory for fluidized bed in three regimes including bubble fluidized bed, fast fluidization and turbulent regimes. These models consider the distribution of the gas flow among emulsion and bubbles and the solid concentration profile often described by an empirical

equation [1, 7]. Most of the modeling works have focused on fuel reactor. The fuel reactor bed is divided into two zones: a dense zone at the bottom of reactor and a freeboard zone above it. The solid distribution in the dense bed is high and roughly constant. In the freeboard zone decay is observed in solid concentration respect to its height. Many researchers used this approach for modeling of reactors in CLC process. Some of these models considered the air reactor, as well. Most of these works focused on bubbling fluidized bed regimes [1].

Abad, et al. [35] developed a model for fuel reactor in chemical looping of CH₄ by CuO impregnated on alumina. The model was validated against data from a 10 kW_{th} unit using a Cu based oxygen carriers. The main model outputs were the solid conversion, the gas composition at the reactor exit, the gas concentration profile in axial direction and the hydrodynamic structure of the reactor. The model results indicate a good agreement with the experimental data. According to these researchers, the results are very sensitive to some parameters such as gas diffusion between emulsion and bubble phase, the decay of solid concentration in the freeboard and the contact efficiency between gas and solids in the freeboard zone. Thus, a simplified model without considering any restriction to gas and solids contacting each other results in an under-prediction at solid inventory by factor of 2-10.

Kolbitsch, et al. [36] considered the diffusion resistance between bubbles and emulsion by using a model parameter which represent an effective amount of solids exposed to gas passing in plug flow ($\varphi_{s,core}$). This parameter encloses different parameters that characterize the gas-solid contact. By adopting this model the performance of a 120 kW chemical looping combustor for combustion of natural gas has been investigated by a Ni-based oxygen carrier. This model describes the behavior of both fuel and air reactor.

Pallares and Johnsson [37] developed a macroscopic model which considered six zones for a large scale CFB reactor. Their findings reveal that there is a good agreement with the experimental data for full scale CFB units. In general, it is found that macroscopic models could be applied for performance analysis, design and optimization of large fluidized bed reactors in a CLC system [1].

5.2. CFD Based Models

A CFD model is based on the first principles of momentum, heat and mass transfer and does not required detailed assumptions in modeling procedure. This model can simulate the behavior of the reactor during a transient time until the steady state is reached. Most of CFD models are developed for reactors in batch mode, without solids circulation, or for small scale CLC systems (300-1,000 W_{th}) [1].

Jung and Gamwo [38] developed a CFD model for fuel reactor modeling in CLC of methane with a Ni based oxygen carrier. They investigated the hydrodynamic behavior of reactor and parameters like longitudinal profiles for reactant and products. Based on their findings, bubble behavior and simulated flow pattern are consistent with the experimental observations.

Deng, et al. [39] conducted a CFD modeling for fuel reactor in CLC process of H₂ by CaSO₄ as oxygen carrier. The distributions of solid volume fraction and gas composition in the reactor are presented. The effects of particle size and bed temperature on

CLC performance predicted, as well. Based on their study the bed temperature is the most important operating parameter affecting the performance of the process.

The presentation of CFD multiphase models for fuel reactor in CLC process is the first step in developing the numerical simulation of such reactors. There is a shortage in literature on modeling of complete loop system. Most of the presented models in literature are developed for fuel reactor modeling and only a few works have been reported on modeling and design of air reactor. It is valuable to couple fuel reactor with other components like the air reactor and cyclone to model full loop system, since the heat integration between CLC reactors is a very significant issue in development of this technology [38, 39]. So far, the most complete modeling 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.

Important progress is made on validating the CFD models with experimental results obtained in small-scale plants using gaseous fuels. But, the relatively complex processes like fluid dynamics, reactivity of the oxygen-carrier, the reaction mechanisms and the effect of solid circulation are not modeled yet using CFD codes in the CLC process which is studied for plants with capacities in of 10-150 kW_{th} range. Based on these drawbacks in CFD modeling development, the macroscopic models are still effective tools for the simulation, design and optimization tasks in CFB technologies [1].

5.3. Reaction Kinetics between Oxygen Carrier and Gas

A CLC process involves gas/solid reactions and the kinetics of these reactions strongly affects the performance and design of corresponding reactors. Thus, the accurate prediction of overall reaction rate based on a correct kinetics is the main and first step in a successful CLC process design. The reaction of an oxygen carrier with a fuel can be described as a non-catalytic gas/solid reaction. The well-known kinetic models used for chemical looping combustion are classified in mainly two categories: nucleation growth, often referred to Avrami-Erofeev model and shrinking core models. The schematic of these two models are shown in Fig. 2 [1-3].

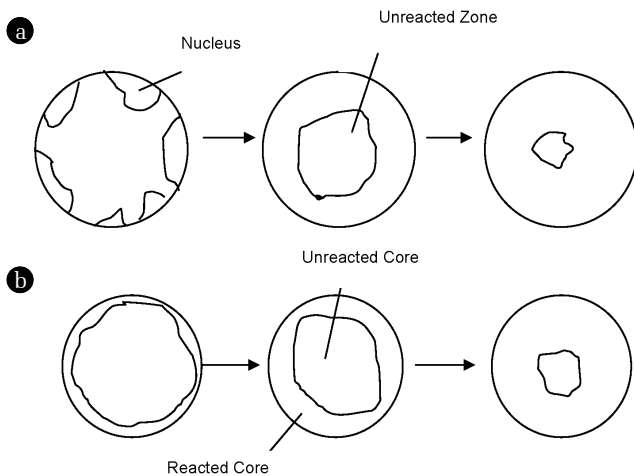


Fig. 2. Kinetic models for gas/solid reaction. (a) Avrami-Erofeev model (AEM) (b) Shrinking core model (SCM).

The nucleation model considers the chemical mechanism and kinetics of the gas-solid reactions only [2]. According to the nucleation and nuclei growth models, the reaction proceeds with the generation of metallic nuclei, which gradually grows and finally overlaps. The reaction rate increases with the number of nuclei during the first moments of reaction, or the induction period. After this period the reaction will occur uniformly over the solid surface, and the reaction front advances uniformly into the inner part of the grain. Thus, the conversions vs. time curves are characterized by a sigmoid behavior, often described by the Avrami-Erofeev Model (AEM) which is based on Eq. (8).

$$\frac{dx_s}{dt} = k'_s(T)C_g^n f(x_s) \quad (8)$$

The general form for the function of solid conversion is described by Eq. (9):

$$f(x_s) = \nu(1 - x_s)[- \ln(1 - x_s)]^{\nu-1/\nu} \quad (9)$$

where, ν is the Avrami exponent [1]. The difference between AEMs is in exponent of ν which is related to the crystal growth dimensions; however, often this coefficient is used as an adjustable parameter. The Random Nucleation Model (RNM) is given by a value of $\nu=1$. When $\nu=1$, an induction period is not present and when $\nu=2$ and 3 the nuclei growth is assumed to be 2-dimensional or 3-dimensional, respectively [3]. This model does not conclude morphological factors, which may be equally important in determining the kinetics. It is observed that the gas-solid reaction rate can be influenced by the grain size for a particle diameter greater than 10 μ m. Especially, for the porous particles, the effect of particle size and its state during the reaction is very important in determining reaction rates.

The unreacted shrinking core model (SCM) takes into account the dependence of particle size and pore structure of the solid reactant particles on the reaction rate. As the reaction progresses the metal-metal oxide surface moves towards the center of particle, leaving behind a porous metallic/metal oxide layer. The gaseous reactants and products must penetrate through this layer [2]. The shrinking core model is developed for different particle shapes including flat plate, cylindrical and spherical particles. These models are expressed in a manner where the conversion rate depends on temperature (T), gaseous reactant concentration (C) and conversion (x). The conversion is defined as the unreacted solid volume divided by the overall reactive particle volume based on Eq. (10) [3].

$$1 - x_s = \left(\frac{r_c}{R_p}\right)^3 \quad (10)$$

where, r_c and R_p are the radius of unreacted core and particle, respectively.

According to the unreacted shrinking core models, a surface separates the solid reactant core from the outer product layer. Initially, the external surface of the solid becomes involved in the reaction. The thickness of the product layer increases with

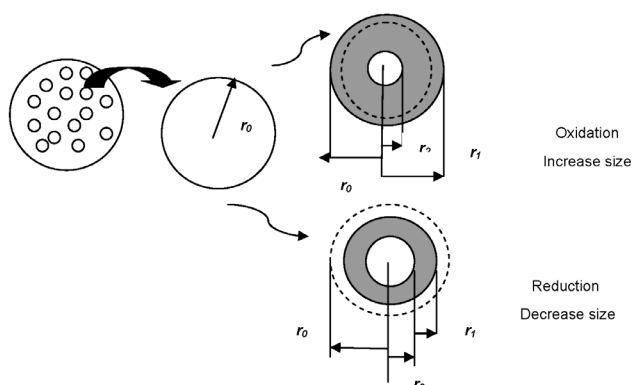


Fig. 3. Schematic of Changing grain size model (CGSM).

time, leaving behind a shrinking core of unreacted solid. Therefore, the heterogeneous reaction proceeds through the three steps: external mass transfer (diffusion through the gas film surrounding the particles), internal mass transfer (diffusion through the product layer and particle pores) and chemical reaction [2]. Frequently, external mass transfer can often be neglected due to the fact that it could be easily eliminated through a sufficient addition of gaseous reactant into the reaction [3].

Changing grain size model (CGSM) is the other frequently used model for modeling of gas/solid reaction kinetic in CLC process. It is in turn a general form of SCM. This model assumes that a solid particle consists of a number of non-porous grains of uniform characteristic length, r_0 . Each grain reacts based on shrinking core model. As the reaction proceeds, the grain size changes, while the unreacted core shrinks. The schematic of the CGSM is shown in Fig. 3.

For most of oxygen carrier particles, the diffusion through the film and product layer presents a negligible resistance and is not considered as controlling step. In this situation, particles can be considered as an agglomerate of individual grains reacting in absence of mass transfer resistance and the conversion is uniform throughout the solid. Therefore, the reaction rate is considered to be independent upon particle size. In this situation, the CGSM model reduced to SCM in grains model (SCMg). On the other word, R_p is substituted by grain radius (r_0) in Eq. (7). The SCMg is successfully used to calculate the kinetic parameters of the reduction and oxidation reactions for Cu-, Ni- and Fe- based oxygen carriers [1].

6. CLC Challenges and Future Prospects

The main issue on developing a CLC process is selection and/or synthesis of a proper oxygen carrier material. The selection of proper active and supporting materials, the preparing methods and condition and the purity of source materials are among the most important factors in synthesis of oxygen carriers. Despite all efforts, there is still a challenge for preparation of an appropriate oxygen carrier with low cost with adequate features for a commercial CLC process.

Modeling of full loop process is still remained as a challenging

issue because of complexity of fluid dynamics, heat and mass transfer processes, contacting patterns and reaction mechanisms. There are few works on process modeling which affect the process design and optimization especially for large scale applications. The scale up of technology which strongly depends on comprehensive understanding of process hydrodynamic is very important issue. More studies should be carried out in this field because CLC is becoming a promising technology in CO_2 capture from fossil fuel at power plants in the future years.

There are many studies with a focus on different aspects of CLC process like issues related to oxygen carriers and reaction kinetics, mass and energy analysis, conventional and modern reactor designs. In addition to power generation applications which use CLC process in its inherent concept, recently some researches are conducted on advanced CLC concepts and technologies related to the new energy applications such as chemical looping solid oxide fuel cell (CLSOFC) and chemical looping air separation (CLAS), see [40].

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