Review

Chemical Looping Combustion: A Brief Overview

Tomasz Czakiert [1],*[ID]**, Jaroslaw Krzywanski** [2][ID]**, Anna Zylka** [2] **and Wojciech Nowak** [3][ID]

[1] Department of Advanced Energy Technologies, Faculty of Infrastructure and Environment, Czestochowa University of Technology, 42-201 Czestochowa, Poland

[2] Division of Advanced Computational Methods, Faculty of Science and Technology, Jan Dlugosz University in Czestochowa, 42-200 Czestochowa, Poland; j.krzywanski@ajd.czest.pl (J.K.); a.zylka@ajd.czest.pl (A.Z.)

[3] Department of Thermal and Fluid-Flow Machinery, Faculty of Energy and Fuels, AGH University of Science and Technology, 30-059 Cracow, Poland; wnowak@agh.edu.pl

* Correspondence: tczakiert@is.pcz.pl

Abstract: The current development of chemical looping combustion (CLC) technology is presented in this paper. This technique of energy conversion enables burning of hydrocarbon fuels with dramatically reduced CO_2 emission into the atmosphere, since the inherent separation of carbon dioxide takes place directly in a combustion unit. In the beginning, the general idea of the CLC process is described, which takes advantage of solids (so-called oxygen carriers) being able to transport oxygen between combustion air and burning fuel. The main groups of oxygen carriers (OC) are characterized and compared, which are Fe-, Mn-, Cu-, Ni-, and Co-based materials. Moreover, different constructions of reactors tailored to perform the CLC process are described, including fluidized-bed reactors, swing reactors, and rotary reactors. The whole systems are based on the chemical looping concept, such as syngas CLC (SG-CLC), in situ Gasification CLC (iG-CLC), chemical looping with oxygen uncoupling (CLOU), and chemical looping reforming (CLR), are discussed as well. Finally, a comparison with other pro-CCS (carbon capture and storage) technologies is provided.

Keywords: CLC; oxygen carriers; reactors; systems

1. Introduction

Carbon dioxide emission from anthropogenic sources, including the power industry, has attracted more and more attention over the last 15 years. This interest brings rapid development of so-called pro-CCS (carbon capture and storage) technologies, which offer the ability to reduce significantly the emission of CO_2 into the atmosphere. As a result, three of these methods, such as pre-combustion capture, post-combustion capture, and oxy-fuel combustion [1–4], have achieved satisfied technological maturity. Nevertheless, commercial implementation on a large scale is still very limited, mainly due to the high energy-efficiency penalty associated among others with ASU (air separation unit) operation [5]. This problem does not concern, however, the innovative technique of chemical looping combustion CLC [6], where solid particles are used to transport oxygen from combustion air to the burning fuel.

The CLC process is usually conducted in a system of two reactors (Figure 1), which consists of the fuel reactor (FR), where combustion takes place, and the air reactor (AR), where oxygen carriers (OC) are regenerated. Thus, oxygen carriers are subjected to continuous oxidation and reduction (Equations (1) and (2)) [7] while they circulate throughout the combined CLC unit. There are two crucial benefits of OCs employment in a power generation system, which are the elimination of conventional energy-consuming air separation units and the inherent separation of forming flue gases (mainly CO_2 and H_2O) from the air supplied to the combustion process. As a result, the flue gas that leaves the fuel reactor is free of atmospheric nitrogen and thus it becomes almost ready for geological sequestration—CCS (carbon capture and storage) and/or commercial utilization—CCU

(carbon capture and utilization) [8]. Concurrently, the exhaust gas from the air reactor consists essentially of nitrogen and the remaining oxygen, which are both environmentally friendly gases.

$$(2n + m)Me_xO_{y-1} + (n + 0.5m)O_2 \rightarrow (2n + m)Me_xO_y \; \Delta H_o \tag{1}$$

$$C_nH_{2m} + (2n + m)Me_xO_y \rightarrow nCO_2 + mH_2O + (2n + m)Me_xO_{y-1} \; \Delta H_r \tag{2}$$
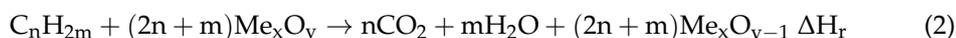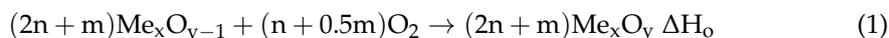
The combined reaction can be shown as Equation (3), where the total amount of heat released in the CLC process is equal to the heat obtained from conventional combustion with gaseous oxygen.

$$C_nH_{2m} + (n + 0.5m)O_2 \rightarrow nCO_2 + mH_2O \; \Delta H_c = \Delta H_o + \Delta H_r \tag{3}$$
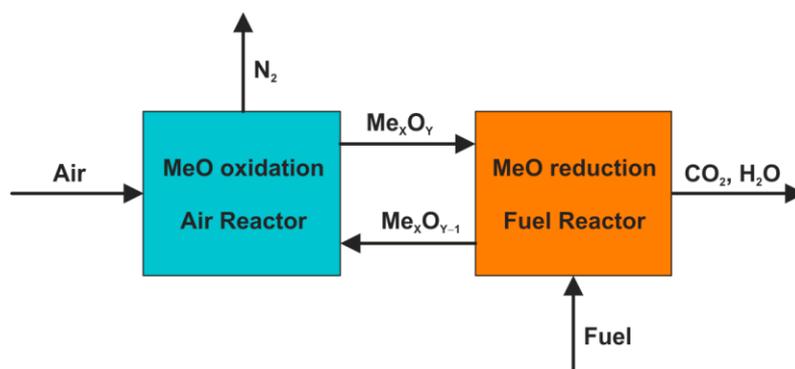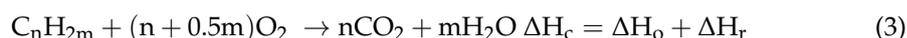
Figure 1. Chemical looping combustion concept.

Therefore, it is obvious that subsequent CO_2 storage [9,10] and/or utilization [11,12] are inseparable from the CLC process since this is the only way to ultimately restrain the greenhouse gas emission into the atmosphere. Generally, there are two major pathways to utilizing CO_2, which include direct and indirect methods. Technologies such as enhanced oil recovery (EOR) [13,14] and enhanced gas recovery (EGR) [15,16], where CO_2 is directly injected underground while enhancing oil or gas recovery, are fully mature and commercially in use. CO_2 can also be utilized in concrete building materials via mineral carbonation, which additionally increases the mechanical strength of these materials. There is also a continuous demand for CO_2 in the food industry (e.g., dry ice, food preservative, and drinks carbonation). However, CO_2 conversion to fuels (methanol, ethanol, syngas, and methane) and chemicals (formic acid and oxalic acid), which is already sufficiently developed technology for full-scale demonstration, seems to be the most promising alternative for the near future. Detailed studies on CCSU (carbon capture, storage, and utilization) technologies can be found elsewhere [17–22].

2. Oxygen Carriers

Solid oxygen carriers behave like red blood cells transporting oxygen in a "blood circulation" of the CLC system where the air reactor acts as "lungs", whereas the fuel reactor resembles "tissue" in which the "organic matter conversion" takes place. Therefore, they become indispensable for proper functioning of the "body" and as their oxygen transport abilities run down the "metabolic" capacities of the whole CLC system disappear.

As described above, solid oxygen carriers (OC) are essential for chemical looping combustion technology. The key features of oxygen carriers, which determine the performance of CLC process include:

- Reactivity with combustibles and oxygen;
- Oxygen transport capacity (OTC);
- Chemical lifetime;
- Mechanical resistance (including melting temperature);

- Tendency to carbon deposition on oxygen carrier surface;
- Toxicity and environmental impact;
- Price and availability.

Oxygen carriers can be classified into several categories. The first one is based on the origin, which means natural OCs (e.g., ilmenite) and synthetic OCs (e.g., $Cu_{0.95}Fe_{1.05}AlO_4$). Another criterion takes into account the number of active compounds (e.g., NiO or $(Mn,Fe)_2O_3$) and their structure (e.g., perovskites [23,24]). Finally, the ability of oxygen uncoupling in an environment of a fuel reactor (CLOU-type OC) is taken into consideration. Recently, very promising novel synthetic oxygen carriers based on geopolymer composites were proposed [25]. The main advantages of geopolymer OCs are, among others, low cost, green synthesis, non-toxicity, and CLOU feature [26]. Furthermore, a good mechanical resistance makes them suitable for fluidized bed applications [27]. In the search for potential oxygen carriers, steel converter slag was also tested with success under circulating fluidized bed (CFB) conditions [28]. Usually, however, solid oxygen carriers are simply divided into five groups, which are: Fe^-, Cu^-, Mn^-, Co^-, and Ni-based OC. Moreover, in addition to metal oxides the supports of different kinds are used, which enriched their inherent properties, among others are: Al_2O_3, $MgAl_2O_4$, TiO_2, SiO_2, ZrO_2, and bentonite.

Key properties of basic oxygen carriers and hence their usefulness in the CLC systems are presented in Table 1. A wide variety of different features can be seen in this chart; therefore, it seems reasonable to use mixed oxygen carriers with selected supports, which should be tailored individually for each chemical looping application. In addition to these data, the comparison of oxygen transport capacity (OTC) is provided for all aforementioned materials as well as for two natural oxygen carriers such as ilmenite and anhydrite (Figure 2). Significant differences can be seen in this figure where the values of OTC vary up to an order of magnitude in general. Much bigger differences relate to the market prices of basic metals (Figure 3), provided by the London Metal Exchange LME (average data for the years 2013–2017). It can be found, for instance, that cobalt is about a hundred times more expensive than iron or manganese and even much more expensive than gypsum compounds. Another crucial factor, which is melting temperature [29], varies from 1084 °C for copper up to 1538 °C for iron [30]. The values of T_m for manganese, nickel, and cobalt are 1244 °C, 1455 °C, and 1495 °C [30], respectively.

$$OTC = \frac{mMn_xO_y - mMn_xO_{y-1}}{mMn_xO_y}$$
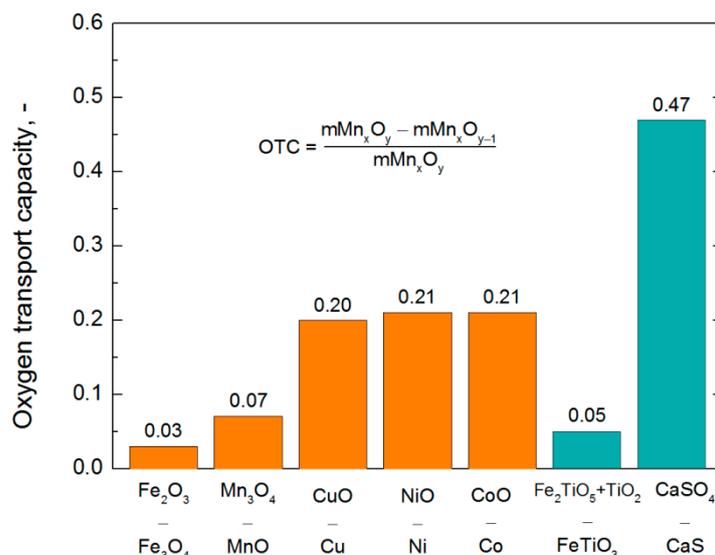
Figure 2. Oxygen transport capacity.

An interesting issue involves the thermal balance over the CLC unit, since the process of oxygen carriers regeneration that takes place in the air reactor appears to be much more exothermic compared with the combustion reactions, which proceed concurrently in the

fuel reactor. Furthermore, the standard heat of reduction reactions with methane and carbon is negative only for Cu-based oxygen carriers [7]. This exposes another crucial function of solid oxygen carriers, which naturally take part in the heat transfer not only to the working fluid but also between the reactors in the CLC system. Safety and environmental issues related to the use of solid oxygen carriers in power generation systems are discussed in detail elsewhere [31,32].

Table 1. Properties of oxygen carriers (based on [33–36]).

	Fe_2O_3/Fe_3O_4	Mn_3O_4/MnO	CuO/Cu	NiO/Ni	CoO/Co
Reactivity with CH_4	low	average	high	very high	low
Reactivity with CO and H_2	average	high	very high	average	low
Oxygen transport capacity	low	average	high	high	high
CLOU effect	no	no [1]	yes	no	no [2]
Cost	low	average	high	very high	very high
Melting temperature	high	average	low	high	high
Health and environment	safe	safe	harmful	very harmful	very harmful

[1] yes, for Mn_2O_3 only; [2] yes, for Co_3O_4 only.
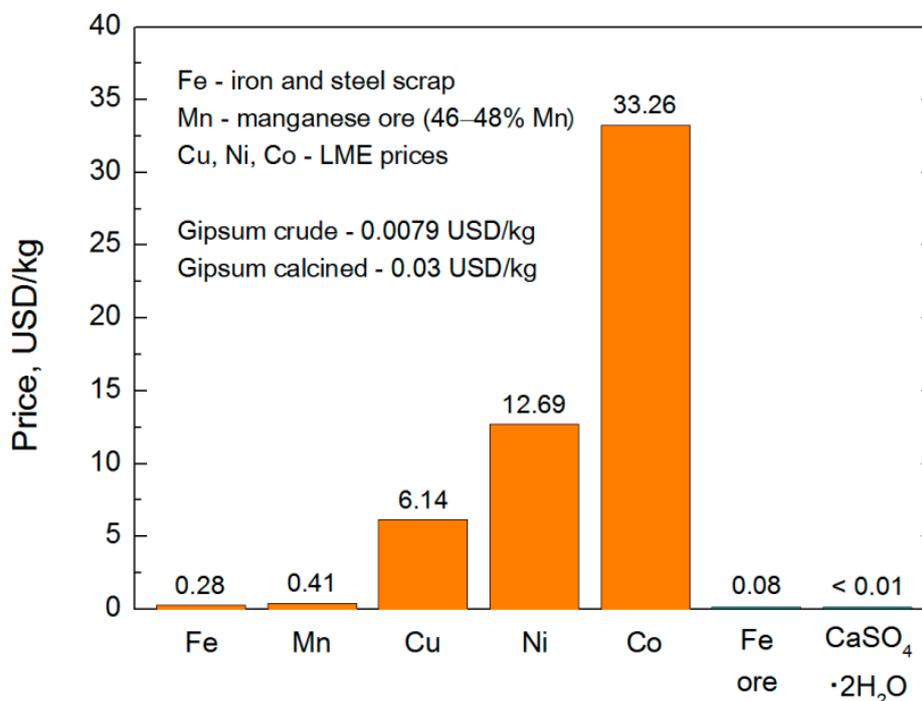
Figure 3. Market prices of feedstocks for oxygen carriers production (based on [37]).

3. Chemical Looping Systems

Several different systems based on chemical looping principles are developed concurrently in order to burn fossil and other fuels in a clean and efficient manner. In a first approach, the whole group of various systems with oxygen carriers [38–43] and so-called carbonate looping systems (with CO_2 carriers) [44,45] can be distinguished. Further classification is presented in Figure 4, which takes into account a feature of oxygen carriers and place of fuel gasification. A somewhat different idea is applied in the chemical looping reforming (CLR) systems [46,47], where fuel conversion is oriented towards hydrogen production.
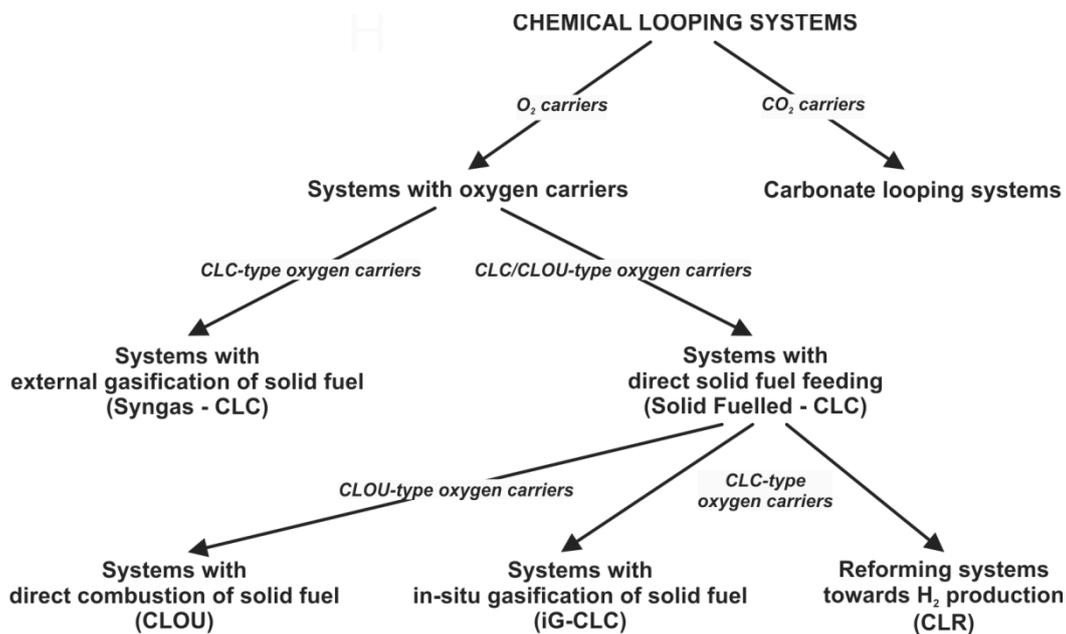
Figure 4. Classification of chemical looping systems.

3.1. SG-CLC System

Originally, the CLC concept was developed for the combustion of gaseous fuel [48,49]. Therefore, for the purpose of solid fuel combustion, the preliminary gasification in an external unit was initially considered, and hence the fuel reactor might be fed directly with a produced syngas. Thus, the proposed Syngas CLC (SG-CLC) system [38,39] exhibits the technical ability of coal conversion in a chemical looping environment (Figure 5), however, it still needs the detached unit for air separation, which is crucial from the economic point of view.
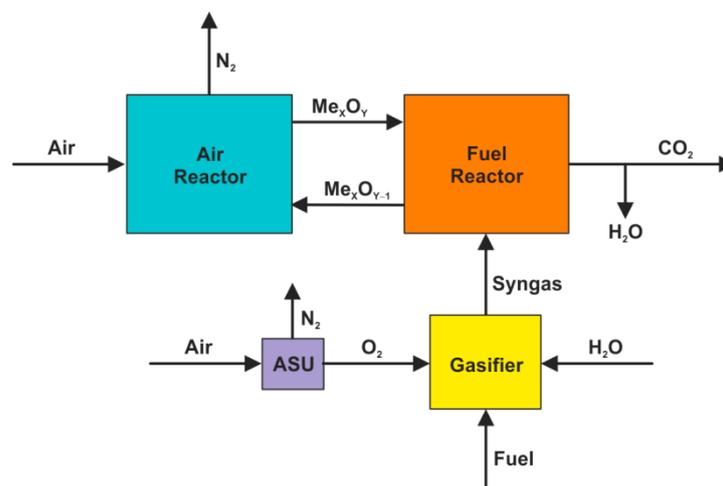
Figure 5. SG-CLC system.

The thermal decomposition of fuel and the gasification of char in a mixture of steam and oxygen proceed according to the following Equations (4)–(6):

$$coal(solid\ fuel) \rightarrow volatiles + char \tag{4}$$

$$char(2C) + O_2 \rightarrow 2CO + Q \tag{5}$$

$$char(C) + H_2O \rightarrow CO + H_2 - Q \tag{6}$$
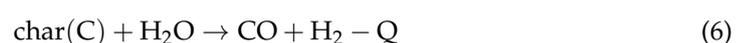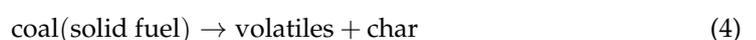
whereas subsequent combustion of volatiles and syngas both being in contact with solid oxygen carriers can be described by the reactions (7) and (8):

$$CO + H_2 + volatiles + nMe_xO_y \rightarrow CO_2 + H_2O + nMe_xO_{y-1} \tag{7}$$

$$CO + H_2O \rightarrow CO_2 + H_2 + Q \tag{8}$$

Concurrently, the reduced oxygen carriers undergo regeneration (Equation (9)) in the air reactor, before they are returned to the combustion zone, which makes the chemical loop complete.

$$Me_xO_{y-1} + 0.5O_2 \rightarrow Me_xO_y \tag{9}$$

3.2. iG-CLC System

For the improved concept called iG-CLC (in situ gasification CLC) [40,41], it was assumed that the gasification process would take place inside the fuel reactor, whereas the recirculated CO_2 might be used as a gasification agent (Figure 6). Thereby, a huge cost associated with both the construction and the operation of an external air separation unit can be eliminated. A weak point appears, however, in a low rate of gasification reactions (6, 10), which slow down the whole combustion process with the use of oxygen carriers.
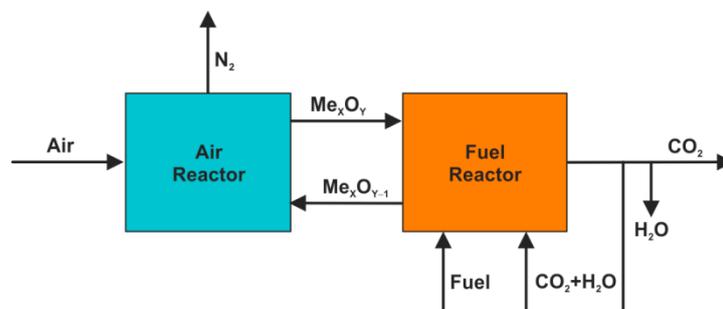

Figure 6. iG-CLC system.

It is also worth mentioning that the exothermic reaction (5) is replaced in the presented system by a Boudouard reaction (10) which, similar to the reaction (6) and the devolatilization process (Equation (4)), has an endothermic nature. In the following stages, the burn out of combustible gases and the oxidation of oxygen carriers run according to the above-given Equations (7)–(9), respectively.

$$char(C) + CO_2 \rightarrow 2CO - Q \tag{10}$$

3.3. CLOU System

New opportunities appeared with the second generation of oxygen carriers (CLOU-type OC), which have the ability to release gaseous oxygen in an environment of the fuel reactor ((Equation (11)). Thus, the initial gasification became less important and the CLOU (chemical looping with oxygen uncoupling) combustion [42,43] (Equations (4), (12) and (13)) starts to resemble essentially the oxy-fuel combustion technology. Therefore, the recirculated carbon dioxide or the mixture of CO_2 and H_2O (in case of "wet" recirculation) fulfils the function of fluidizing gas in the unit (Figure 7) rather than the gasification agent as described previously.

$$2M_xO_y \leftrightarrow 2Me_xO_{y-1} + O_2 \tag{11}$$

$$char(C) + O_2 \rightarrow CO_2 + Q \tag{12}$$

$$volatiles + O_2 \rightarrow CO_2 + H_2O + Q \tag{13}$$
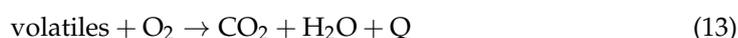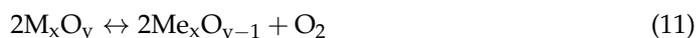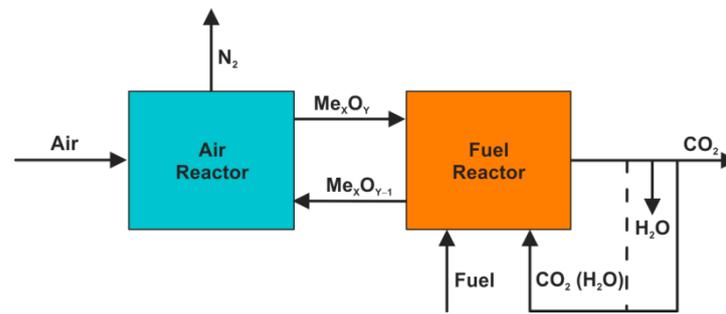
Figure 7. CLOU system.

It can be claimed thereby that the intensive investigations focused on inexpensive oxygen carriers with increased O_2 transport capacity, improved reactivity, and high mechanical strength are currently of great importance for further accelerated development of the chemical looping combustion technology.

3.4. CLR System

Another interesting concept based on the chemical looping idea is oriented towards hydrogen production and it is widely known as chemical looping reforming (CLR) [46,47]. Two different techniques can be found under this name, which are Dry CLR and Steam CLR, where the fuel reactor is supplied with CO_2 or H_2O, respectively (Figure 8). Concurrently, oxygen is provided to the fuel reactor with the use of solid oxygen carriers and hence the whole gasification process can be described by the Equations (4) and (14) together with Equation (10) in the case of Dry CLR or Equation (6) for the steam-reforming method.

$$\text{volatiles} + \text{char} + n\text{Me}_x\text{O}_y \rightarrow \text{CO} + \text{H}_2 + n\text{Me}_x\text{O}_{y-1} \tag{14}$$
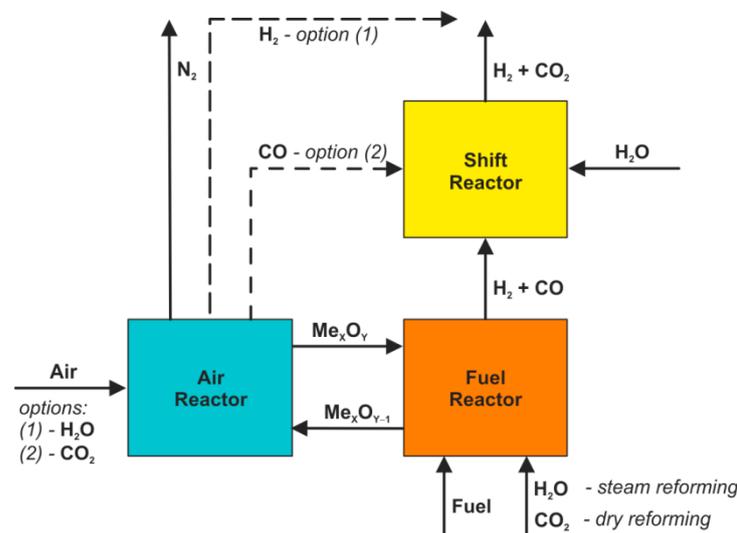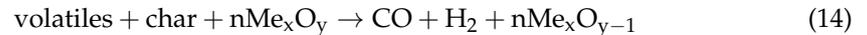
Figure 8. CLR system.

In the second stage, the products of aforementioned Equations (6), (10) and (14) are directed from the fuel reactor to the shift reactor (SR), where CO is converted into CO_2 according to the following Equation (15):

$$\text{CO} + \text{H}_2 + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}_2 \tag{15}$$
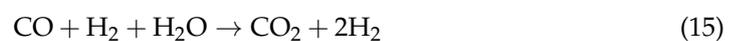
Moreover, two additional options are considered for the regeneration of oxygen carriers, which take into account the use of steam (Equation (16)) or CO_2 (Equation (17))

instead of air (Equation (9)) that is usually utilized for this purpose in the air reactor (see: Figure 8).

$$Me_xO_{y-1} + H_2O \rightarrow Me_xO_y + H_2 \qquad (16)$$

$$Me_xO_{y-1} + CO_2 \rightarrow Me_xO_y + CO \qquad (17)$$
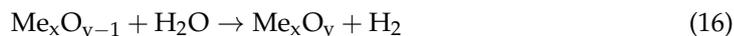
The biggest challenge seems to be, however, the selective oxygen carriers, which react very easily with carbon (conversion to CO) rather than with hydrogen and initially generated carbon monoxide. A very narrow group of such materials includes, among others, some ferrites (e.g., $CaFe_2O_4$ or $BaFe_2O_4$) [50,51]. It is also worth mentioning that the gasification reactions can be accelerated by the catalysts (e.g., Ni-Fe composites) [52,53] introduced directly into the fuel reactor, which is distinguished as a catalyst-assisted CLR technique. The results of the experimental investigations on CLR can be found in [54–57].

4. Chemical Looping Reactors

Generally, three basic constructions of reactors are considered in order to put the idea of chemical looping combustion into practice, which are as follows:

- Dual fluidized-bed reactors [33,58,59];
- Swing reactors or fixed (packed) bed reactors [60,61];
- Rotary (rotating bed) reactors [62,63].

Each aforementioned design certainly has its advantages and disadvantages. Similarly, one has a facility for gaseous fuel combustion while the other can be easily adapted to burn solid fuels. Nevertheless, every construction should meet three common criteria, which finally affect the operation efficiency of the CLC unit. The first one concerns maintaining the oxygen carriers-to-fuel ratio by means of an appropriate recirculation rate (fluidized-bed reactors), oxidation–reduction sequence (swing reactors), and rotational speed (rotary reactors). Another issue involves the sufficient residence times of oxygen carriers in both air and fuel reactors, which influence the combustion process as well. The last question relates to the efficient capture of CO_2, which is executed by the effective sealing of the sections with fuel conversion and oxygen carriers regeneration. This prevents gas (particularly CO_2) from leaking between AR and FR as well as from char slipping into the air reactor.

4.1. Dual Fluidized-Bed Reactor

Most of the CLC reactors presented in the literature are dual fluidized-bed (DFB) reactors [33,58,59] of peculiar design. This is due to the high efficiency of fuel conversion of these reactors and their ability to burn solid fuels. Other advantages of this kind of reactor is the suitability for scaling-up [64,65], high throughout output capacity, and smooth operation [66]. On the other hand, the construction of DFB reactors is more sophisticated and hence the operation appears to be more demanding compared with other designs mentioned above. Moreover, the mechanical attrition caused by moving particles may lead to serious problems, which are common for circulating fluidized bed units in general.

A dual fluidized-bed reactor consists of two combined reactors, which are the fuel reactor and the air reactor (Figure 9). The fuel reactor is fed with fuel being burnt with the help of oxygen carriers, which are further regenerated in the air reactor. Solids circulation becomes possible due to the cyclone separator and two loop-seals installed between the reactors. Usually, the air reactor is operated under fast-fluidized bed (FFB) conditions, whereas the fuel reactor works in a regime of bubbling fluidized bed (BFB), however, there are known constructions with FFB [67,68] or BFB [69] in both reactors. Moreover, CLC reactors are often equipped with a so-called carbon stripper (CS) system and/or oxygen polishing (OP) system, both shown in Figure 9. The carbon stripper [70–72] is used to return unburned char back to the fuel reactor, whereas oxygen polishing [73,74] enables to burn out all combustibles remaining in the exhaust gases.
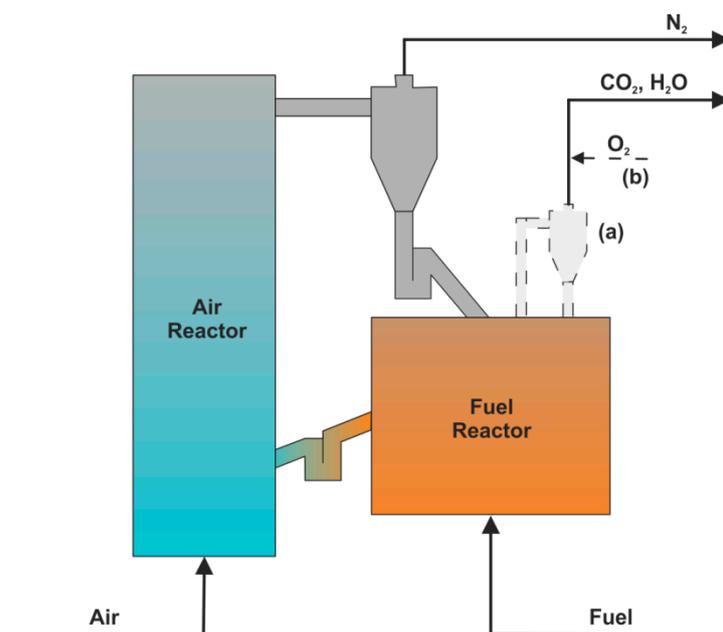
Figure 9. Dual-fluidized bed reactor for chemical looping combustion; optional systems: carbon stripper (a) and oxygen polishing (b).

Whitty et al. [75] preformed CLOU experiments in a 200 kWth dual-fluidized bed reactor. Authors point to the main challenges as balancing oxygen supply to the fuel reactor, heat generation, and temperatures, as well as global and internal circulation rates. Low CO_2 capture efficiency was noticed on a 1 MWth pilot-scale CLC unit with two interconnected CFB reactors using ilmenite as oxygen carrier and hard coal as fuel [76]. Authors found that unconverted char left the fuel reactor and burned in the air reactor. The reason for this is that no carbon stripper was used during these investigations. A different operational strategy based on the fuel reactor staged fluidization without a carbon stripper is proposed by Shen et al. [77,78]. It was proved that internal distributors in a multistage fuel reactor sufficiently improve carbon conversion and CO_2 capture efficiencies. The main difficulties with biomass fuel utilization in CLC reactors are mentioned by Gogolev et al. [79]. The authors indicate the bed agglomeration, oxygen carrier deactivation, fouling, and corrosion as the most harmful effects associated with biomass alkali release. The problem of gas leakages between fluidized bed reactors via a loop seal was investigated by Lindmuller et al. [80] on a 25 kWth CLC facility. Loop seal design ideas and operation condition proposals are suggested in this work. Very useful guidelines were provided by Zhao et al. [81], who described long-term operational experiences from the interconnected fluidized bed reactors of different scales. Further details on the performance of a 50 kWth coal-fueled chemical-looping combustor can be found in [82]. Another excellent work of Lyngfelt et al. [83] was published recently, which summarizes over 10,000 hours of chemical looping combustion tests carried out around the world. The authors identify a major difficulty with the scaling-up of the CLC process to commercial use, which is the lack of incentives for CO_2 capture and the risk in general. Therefore, the multipurpose dual fluidized bed (MDFB) concept for maximum flexibility is proposed among others. Operational experiences and practical challenges of the fluidized-bed units are also presented in other research works [84–98].

4.2. Swing Reactor

Another type of reactor that can be employed for chemical looping combustion is a swing reactor (fixed/packed bed reactor) [60,61]. Simple design and easy operation are the main advantages of this construction. Moreover, the ability of chemical looping performance under elevated pressure [99,100] seems to be an additional benefit as well. A

weak point of swing reactors is, however, the readiness for gaseous fuel combustion only, therefore, in the case of solid fuels they need to be gasified in advance (see: SG-CLC system).

The single module of the swing reactor consists of two columns placed in parallel, both filled up with solid oxygen carriers (Figure 10). While the first column (FR) is fed with fuel, the second one acts as the air reactor. After the bed in the fuel reactor is depleted and the oxygen carriers in AR are re-oxidized, the roles are reversed. Thus, the CLC process becomes cyclical. Between the following stages, the columns are purged, which consumes energy and causes interruptions. Therefore, the system of several smaller modules rather than one large unit is recommended for the continuous and smooth operation of the whole CLC system.
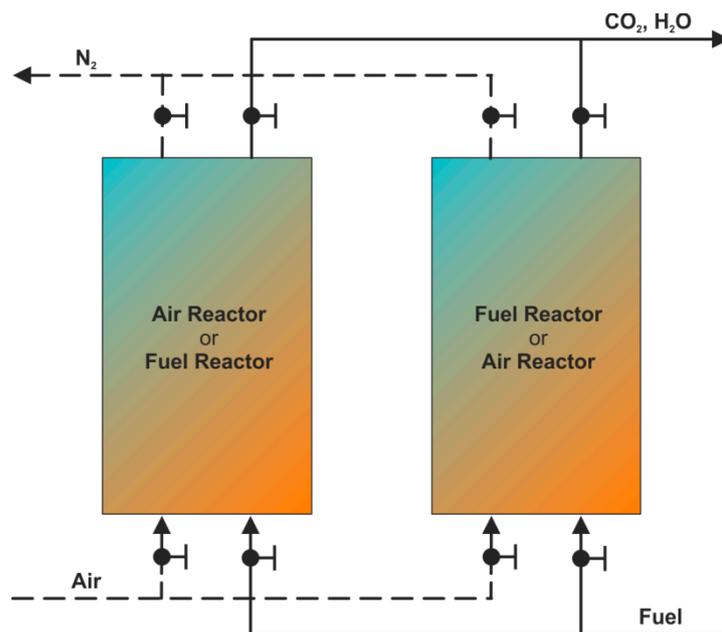

Figure 10. Swing reactor.

Han and Bollas [101] explored the use of a reverse-flow in a fixed-bed reactor fueled with methane and syngas. The authors found that periodic reversal of gas flow direction enhances the contact between the fuel and unconverted oxygen carriers, improves temperature distribution in a bed and conversion uniformity, as well as suppresses carbon deposition on NiO oxygen carriers. It was also emphasized that fixed-bed design avoids the issue of attrition and gas–solid separation typically found in circulating fluidized bed units. The problem with excessive carbon deposition on ilmenite oxygen carriers was also mentioned by Gallucci et al. [102]. The experimental results showed, however, that the use of wet syngas as fuel and the increase in operating pressure enables to eliminate this unfavorable phenomenon. It was concurrently demonstrated that pressurized CLC can be easily accommodated in fixed-bed reactors. In another work [103], a fixed-bed reactor was employed for the tests with bimetallic Cu–Fe–Si oxygen carriers at various operating conditions. The authors state that optimized OC to fuel ratio is the key to avoiding solids agglomeration caused by copper at higher temperatures. The combustion of CO and CH_4 with the use of ilmenite as the oxygen carrier in packed fluidized bed reactor was recently investigated by Nemati and Ryden [104]. The results show that random packings in a packed fluidized bed can significantly improve fuel conversion in comparison with an ordinary bubbling bed without packings. The authors believe that this improvement results from more efficient gas–solid mass transfer due to the reduced bubble size. Detailed results from experimental tests on fixed bed reactors are reported in [105–110].

4.3. Rotary Reactor

Rotary reactors [62,63] are not investigated often compared with dual fluidized-bed reactors and swing reactors, despite a relatively high efficiency of fuel conversion. The biggest challenge in construction and operation of rotary reactors appears to be, however, the sealing of the following sections and parts being in continuous motion. These difficulties lead primarily to lower efficiency of CO_2 capture as well as lower purity of exhaust gases. Moreover, this type of CLC unit is destined for gaseous fuel only.

A rotary reactor (Figure 11) is made of three coaxial rings, from which internal and external rings are fixed to each other while the central ring revolves incessantly in one initially set direction. Moreover, the whole unit is divided into four sections, including the air section, fuel section, and two curtain sections. The central ring is packed with solid oxygen carriers. Fuel and air together with purging gas are fed into the appropriate sections of the internal ring, whereas flue gas and exhaust gases are taken off from the external ring, respectively. Thereby, the concept of the rotary reactor combines certain features of both the dual-fluidized bed reactor (continuous operation, oxygen carriers "circulation") and swing reactor (fixed/packed bed).
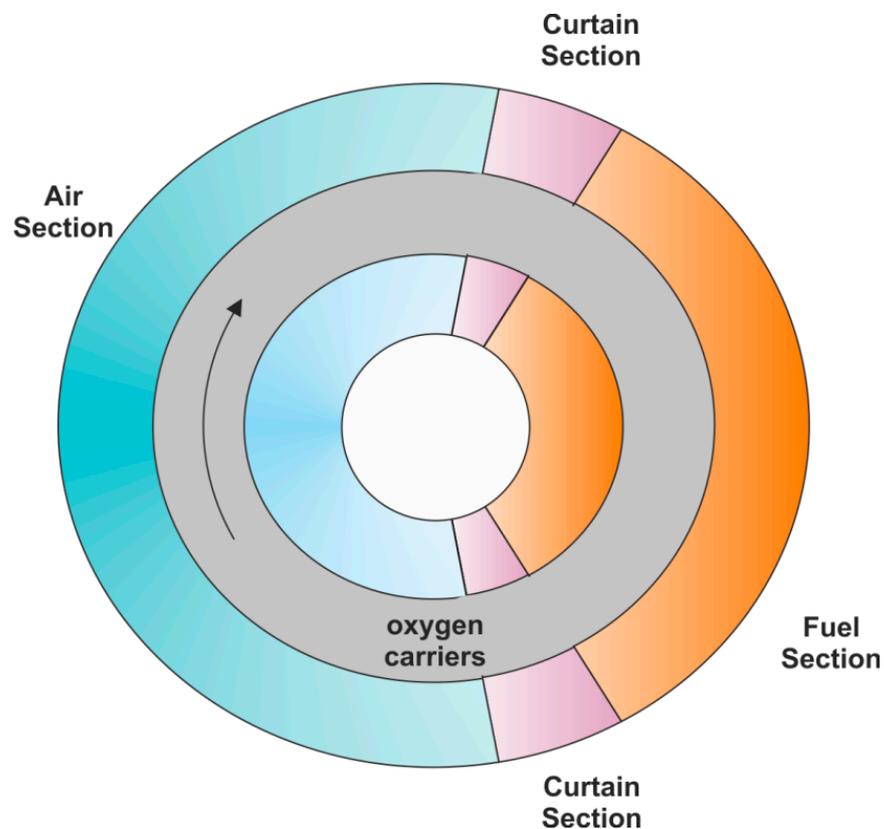
Figure 11. Rotary reactor.

Iloeje et al. [111] noticed that one of the main operational problems associated with solid oxygen carriers' circulation in DFB constructions, which is the mechanical attrition, is naturally eliminated in rotary reactors. In another work [112], the authors evaluated the rotary reactor design for copper, nickel, and iron-based oxygen carriers. Researchers define practical challenges as proper selection of reactor geometry, rotating speed, and gas flow rates, which influence efficient fuel conversion and CO_2 separation. The authors claim, however, that low rotation speed and appropriately selected seals can minimize gas leakages during reactor operation. The problem with air slipping to the fuel section was also observed by Hakonsen and Blom [113] in their prototype rotating bed reactor, which finally results in low purity of captured CO_2. Other results presented by Zhao and Ghoniem [114] confirm that the geometry of the rotary reactor and the operating conditions

will depend preliminary on the oxygen carrier properties. The OC kinetics together with the inlet gas temperature and the operating pressure are identified as the most important factors in this work.

5. Competitiveness of CLC Technology

Chemical looping combustion technology offers almost pure carbon dioxide at the outlet of the reactor, without any additional installations for gas separation. Therefore, dramatic reduction in CO_2 emission into the atmosphere becomes possible with lower operating and capital expenditures (OPEX and CAPEX, respectively) related to the whole power system [115,116]. Near-zero emission takes place when captured CO_2 is subsequently stored or utilized, which is described at the begging of this paper, however, even negative CO_2 emission is possible if only biomass is used as fuel [117,118]. Thus, the CLC technique with its inherent separation appears to be competitive for other pro-CCS technologies, which need advanced air separation units (oxy-fuel combustion and pre-combustion capture) or post-processing CO_2 capture unit (post-combustion capture). The comparison of selected factors determined for both the CLC reactor and conventional circulating fluidized bed (CFB) boiler integrated with post-combustion CO_2 scrubber using monoethanolamine (MEA) is presented in Table 2 [119,120]. Moreover, the authors claim that the results of analyses carried out for the CFB-MEA case and the OXY-CFB case are very similar. The key difference between a reference case (conventional CFB unit) and other examined pro-CCS technologies is the CO_2 capture facility, which significantly affects the net efficiency and other indices of the so-called near-zero emission power plants. A considerable discrepancy (more than 5 percentage points) between the net efficiencies of the CLC reactor and the CFB-MEA unit can be seen, which results mainly from the operation of the CO_2 scrubbing system. Consequently, the energy penalty affects the cost of electricity production, which is also shown in this chart. Another issue is the CO_2 avoidance cost, which is higher by 16 EUR/t_{CO2} for the CFB-MEA unit which means a significant increase of about 43%.

Table 2. Comparison of chemical looping combustion technology (CLC) with the amine absorption method (MEA30%) with reference to a 630 MW_e power unit with a fluidized bed boiler (CFB) (based on [119,120]).

	CFB Unit (Reference)	MEA 30%	CLC
Net power, MW_e	630	630	630
Net efficiency, %	44.9	34.9	40
Coal consumption, t/h	198	255	222
CAPEX, M EUR	1215	2064	1785
OPEX, M EUR	156	220	206
Cost of electricity, EUR/MWh	63	98	88
CO_2 avoidance cost, EUR/t_{CO2}	-	53	37
CO_2 capture rate, %	-	>90	>90

The comparison of the SG-CLC concept with the pre-combustion CO_2 capture technology can be found in [116]. The net efficiency of 39.7% was determined for the CLC unit, which is about 2.6 percentage points more compared with the plant with the pre-combustion CO_2 capture. Furthermore, the CO_2 capture efficiency significantly exceeds the level of 90% in both evaluated cases. As a reference, a conventional integrated gasification combined cycle (IGCC) of the same fuel input energy (1127 MWth) was established, for which the net efficiency reaches 44.3% as it is not burdened by any CO_2 capture systems. Very promising results can be also found in [121], where the achieved net efficiency penalty is less than one percentage point for the integrated system of the CLOU reactor and CHP plant in comparison with the conventional reference plant with the same fuel input. Furthermore, the use of biomass as fuel allows the combined production of heat and power with the so-called negative emission of CO_2. The potential of biomass combustion in the CLC plant with CCS is also noticed by Keller et al. [122]. In this study, chemical looping

combustion is benchmarked against a CFB process with post-combustion CO_2 capture by amine scrubbing. The authors estimate, among other things, that for the plant of 50 MWth HHV fuel input, a cost reduction in the entire CLC-CCS chain can reach 17% over the CFB reference plant with an amine-scrubbing post-combustion capture process. Another interesting evaluation of a poly-generation solar-assisted natural gas-fired CLC plant with waste heat utilization using absorption chilling for cooling purposes was carried out by Ogidiama et al. [123]. The authors claim that exhaust heat utilization significantly improves the overall efficiency of the combined power and cooling plant, which can exceed 63%. Furthermore, the integration with the solar system results in higher flexibility of the entire CLC plant. Other comprehensive techno-economic analyses of chemical looping combustion technologies can be found elsewhere [124–133]. The most recent study on a 550 MW_e brown coal-fired CLC power plant is provided by Sayeed et al. [134]. The net efficiency penalty of slightly more than five percentage points was obtained for a deeply integrated CLC system in comparison with a conventional supercritical pulverized coal-fired power station of the same net output. In conclusion, the authors state that for a considered commercial-scale CLC power plant with 90% CO_2 capture, an increase in the cost of electricity can be lower than 35%, which enables to meet the USDOE's (United States Department of Energy) target.

6. Conclusions

A rising technology of chemical looping combustion (CLC) has untapped potential to be used in zero CO_2 emission power generation systems. The inherent separation that takes place in the CLC reactors results in a highly reduced internal load of the plant, and hence the CLC technology can compete with other pro-CCS technologies such as oxy-fuel combustion, pre-combustion capture, and post-combustion capture. However, it is still not mature enough for commercial implementation.

Key properties of currently considered oxygen carriers are provided, from which the CLOU feature seems to be crucial regarding direct solid fuel combustion. Innovative OCs as geopolymer composites are also mentioned. Various kinds of chemical looping systems are presented including those with external and internal gasification as well as one with direct combustion of solid fuels. Moreover, different designs of CLC reactors are shown including dual fluidized-bed construction, which gives the best prospects for further development of chemical looping combustion technology.

It is also noticed that ultimate utilization of the generated CO_2 is essential for this concept, however, geological sequestration seems to be also necessary due to the global volume of greenhouse gas emissions. The greatest capabilities have EOR and EGR technologies, but the production of carbon-based fuels and other chemicals appears to be of great importance at present.

Nomenclature

AR	Air reactor
ASU	Air separation unit
BFB	Bubbling fluidized bed
CAPEX	Capital expenditures
CCS	Carbon capture and storage
CCSU	Carbon capture, storage, and utilization
CCU	Carbon capture and utilization
CFB	Circulating fluidized bed
CLC	Chemical looping combustion
CLOU	Chemical looping with oxygen uncoupling
CLR	Chemical looping reforming
CS	Carbon stripper
DFB	Dual fluidized bed
EGR	Enhanced gas recovery
EOR	Enhanced oil recovery
FFB	Fast fluidized bed
FR	Fuel reactor
IGCC	Integrated gasification combined cycle
iG-CLC	Incsitu gasification chemical looping combustion
MDFB	Multipurpose dual fluidized bed
MEA	Monoethanolamine
OC	Oxygen carrier
OP	Oxygen polishing
OPEX	Operating expenditures
OTC	Oxygen transport capacity
OXY	Oxy-fuel combustion
SG-CLC	Syngas chemical looping combustion
SR	Shift reactor
USDOE	United States Department of Energy

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