Negative CO₂ emissions through the use of biofuels in chemical looping technology: A review.

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Abstract

In order to limit the increase in the global average temperature to 2 °C or below, the Paris Agreement proposed the reduction of CO₂ emissions throughout this century. Bioenergy with CO₂ capture and storage (BECCS) technologies represent an interesting option in order to allow this goal to be metgoal, because they are able to achieve negative CO₂ emissions. Chemical looping (CL) is recognized as one of the most innovative CO₂ capture technologies owing to its low energy penalty. CL processes permit the utilization of renewable fuels in a nitrogen-free atmosphere, given that the required oxygen is supplied by solid oxygen carriers. The present work presents an overview of the status of development of the use of biofuels in chemical looping technologies, including chemical looping combustion (CLC) and chemical looping with oxygen uncoupling (CLOU) for the production of heat/electricity, as well as chemical looping reforming (CLR), chemical looping gasification (CLG) and chemical looping coupled with water splitting (CLWS) for syngas/H₂ generation. The main milestones in the development of such processes are shown, and the future trends and opportunities for CL technology with biofuels are discussed.

Keywords: negative CO₂ emissions; BECCS; biofuels; CO₂ capture; chemical looping.

1. Introduction

Reducing anthropogenic emissions of CO₂ has become one of the main environmental concerns at present, as links have been found between the increase in CO₂ levels in the atmosphere and the increase in global warming. At the 21st Conference of Parties (COP-21) of the United Nations Framework Convention on Climate Change (UNFCCC) held in Paris in 2015, 194 countries signed the Paris Agreement, whose goals are to hold the increase in the global average temperature to well below 2 °C by 2100 and to pursue efforts to limit the temperature increase to 1.5 °C above preindustrial levels [1]. The Paris Agreement came into force on 4

November 2016 and currently it has been ratified by 179 countries accounting for 88.75% of total greenhouse gas emissions [2]. Several actions must be promoted if the proposed aim is to be achieved. Measures traditionally considered for the reduction of CO₂ emissions into the atmosphere [3], such as improvement in the use and generation of energy, continued use of nuclear energy, boosting energy generation from renewable sources and CO₂ capture, are not sufficient to limit the CO₂ concentration in the atmosphere to the desired levels. In fact, the adoption of new solutions capable of removing CO₂ from the atmosphere, referred to as “negative emission technologies (NETs)”, will be necessary in the near future. The increasing interest to find innovative solutions that allow reaching below zero CO₂ emissions has recently led to the celebration of the first international meeting on NETs [4]. According to predictions by the United Nations Intergovernmental Panel on Climate Change (IPCC), CO₂ emissions should peak by 2020 and then decrease to negative values by the end of the century [5]. Among the different options, most low-carbon scenarios rely on the integration of CO₂ capture and storage (CCS) technologies with the use of renewable fuels such as biofuels, known as bioenergy with CO₂ capture and storage (BECCS) [6-9]. Fuss et al. [10] developed a detailed literature review on the different options to remove carbon from the atmosphere using NETs. They focused on seven technologies, i.e. bioenergy with carbon capture and storage (BECCS), afforestation and reforestation, direct air capture and storage, enhanced weathering, ocean fertilisation, biochar and soil carbon sequestration. From a systematic review of the literature available, they estimated the global negative emissions potential in 2050 for the seven options. They related this potential with the negative emissions cost, deployment potential and key-side effects. According to their findings, among all the options BECCS technologies represent a good compromise between carbon removal potential (0.5-5 GtCO₂ yr⁻¹) and CO₂ removal costs 100-200 US\$ per t CO₂.

The BECCS concept was proposed at the beginning of the present century as a response to the evidences on climate change [11, 12]. Some studies identified in BECCS the potential to

remove CO₂ from the atmosphere at a scale that, together with other mitigation options, could help deliver pre-industrial CO₂ concentrations [13, 14] while allowing for global economic growth [15]. In a comprehensive recent review on the perspectives in the research and regulation of bioenergy deployment, Creutzig et al. [16] identified the strengths of BECCS in long-run mitigation. First, BECCS can be applied to a wide range of technologies with different range of CO₂ emissions e.g. power plants, industry, biomass refineries or biomass gasification plants [17]. Second, the potential for negative emissions of BECCS may allow reaching the goals in CO₂ emission reductions in time. Moreover, considering BECCS as part of the technological options for CO₂ emission reduction, less near-term emission reductions are required. Third, negative emissions from BECCS can compensate in the second half of the 21st century for residual emissions in other sectors, such as industrial (pulp and paper, cement, iron and steel) or transport (including aviation). However, some controversy has risen regarding the deployment of BECCS technology. Considering the side-effects, BECCS is one of the NETs with the largest demand for land. This can compromise both the extent of negative emissions if greenhouse gas emissions from biomass supply chain are also considered [17] and also food production, biodiversity and land to be used for other purposes [18]. Therefore, the use of marginal land as well as waste biomass feedstocks will benefit BECCS implementation. It will be then important to assess the bioenergy resources available in different locations. Several examples can be found in literature about the use of the evaluation of BECCS potential of different regions. Australia is focused on organic waste from the municipal, agricultural, and forestry sectors [19]. A recent techno-economic and environmental impact studies were conducted for four BECCS options; landfill gas combusted in a gas turbine, bagasse and forest residue and municipal solid waste. Brazil identified the possibility of cost-effective negative emissions in the joint production of ethanol and electricity based on sugar cane, bagasse and other residues [20]. In Nordic countries (Finland, Sweden and Denmark) biomass potential per capita is one of the largest in the world which facilitates the development of BECCS based on

biomass [21]. The use of domestic forest biomass as bioenergy source is also considered as an option in Korea [22] and in Austria [23]. In North America, BECCS based on forestry, wastes, agricultural residues and dedicated energy crops can enable a carbon-negative power system in western North America by 2050 with up to 145% emissions reduction from 1990 levels [24].

Fig. 1 is a schematic of the BECCS concept. In order to achieve negative CO₂ emissions, the captured CO₂ must be stored (CCS), i.e. isolated from the atmosphere for long periods.

Among the preferred options is the injection of CO₂ at supercritical conditions within deep saline aquifers [3]. However, the use of CO₂ to produce synthetic fuels or chemical products, such as plastics, has recently attracted great attention. In this case, renewable energy (wind, solar) can be used to upgrade CO₂. The bio-source of carbon in the captured CO₂ can benefit the carbon balance in the atmosphere when biofuels are used with CO₂ capture and utilization (CCU) [25]. Today, the experience of BECCS technologies at scales necessary for climate mitigation is limited. Besides technical issues, there are also other side effects influencing the widespread of BECCS [26]. Table 1 summarizes the global status of BECCS worldwide showing the operational projects [17]. In the next five years, three more projects are expected to start operation and seven more are under evaluation.

The development of BECCS will influence the bio-energy markets. Without BECCS most of the bioenergy is used in the transport sector. With BECCS, bioenergy can be also used in the power [27] and in the industrial sector [28] which is where CO₂ capture and storage (CCS) technologies have been intensively developed over the last 20 years, leading to their current technical readiness level (TRL) grading of 7, with scale-up likely in the short-medium term [29]. All these technologies are intended to produce a concentrated CO₂ stream during the fuel combustion process, which can be captured and safely stored, therefore preventing CO₂ emission into the atmosphere.

Fig. 2 is a schematic of the BECCS concept including the options for CO₂ capture and further storage or use. Most of the advanced CO₂ capture technologies involve post-combustion, oxy-

combustion and pre-combustion [3]. Post-combustion and oxy-combustion processes consider the combustion of the carbonaceous fuel with the eventual objective of obtaining a pure CO₂ stream from the combustion gases. Therefore, these technologies are preferred for implementation in large combustion plants. On the contrary, de-carbonization of the fuel is performed in pre-combustion processes, where syngas and CO₂ are generated and separated from each other. Syngas (CO+H₂) can be converted into liquid hydrocarbons, via the Fischer-Tropsch process, or into pure hydrogen. In this case, H₂ can be considered a clean energy vector, contributing to the mitigation of global warming if the captured CO₂ is not emitted to the atmosphere. The use of these green hydrocarbons and H₂ in the transport sector could be highly significant, as this sector is a major contributor to anthropogenic CO₂ emissions [5]. Finally, two different options can be considered for the captured CO₂. Given the renewable origin of the fuel, negative emissions can be achieved if this captured CO₂ is safely sequestered (CCS). In contrast, neutral emissions would be achieved if a CCU process is used.

In any case, these technologies require a CO₂ separation step for post-combustion and pre-combustion, or the separation of O₂ from air in oxy-combustion, which imply high economic and energy costs. In this sense, chemical looping processes have emerged in recent years as a competitive option because of the intrinsic CO₂ capture in the process [30]. In fact, CL processes provide the best cost reduction benefit from among the various current and envisioned CCS technologies in a carbon-constrained scenario, according to the US Department of Energy's road map [31]. Moreover, in Europe, the Energy Technologies Institute of the UK commissioned the Techno-Economic Study of Biomass to Power with Integrated CO₂ Capture (TESBIC) [32], a study that compared 28 different potential combinations of CCS technologies (solvent scrubbing, oxyfuel, integrated gasification combined cycle (IGCC) and other advanced technologies). It concluded that chemical looping was a highly competitive technology, with the lowest potential cost of CO₂ reduction among the technologies considered.

In the combustion of solid fuels, the costs of the CO₂ avoided is usually estimated around 30–50 €/t CO₂ for the state of the art technologies [33, 34], while 17 €/t CO₂ is estimated for the chemical looping combustion (CLC) process [35]. Later, Cormos [36] evaluated the potential of the CLC process for various solid fuels, including both fossil and renewable ones, in comparison with the conventional combustion and other CO₂ capture technologies such as gas-liquid absorption or oxy-combustion. Considering a 100 MWe power plant, this author found that CLC systems for solid fuel cases have lower electricity costs (85–92 €/MW h) as well as CO₂ capture costs (24–27 €/t CO₂ avoided cost) than other conventional technologies (90–110 €/MW h and 35–60 €/t CO₂ avoided cost). For the same size of power plant, the use of sawdust as fuel resulted in the same cost order as the use of coal. In addition, the energy penalty for CLC with solid fuels is usually estimated at 2-3 %, which is significantly lower than the energy penalty in the 7-9% interval estimated for other CO₂ capture technologies [37]. Recently, an energy efficiency of 46.8% has been estimated for the combustion of biomass with >99% CO₂ capture [36]. Note that the CO₂ avoided in other technologies is lower than in CLC, with values of about 90 % in the optimized condition. Besides, Lyngfelt recently highlighted the challenges and opportunities of CL technologies with biofuels within BECCS not only in the reduction of costs and the increase in the overall efficiency of power generation, but also considering other aspects such as: i) extension of the range of possible fuels which can be utilized and ii) reduction of the NO_x emissions [38].

Chemical looping technologies are also an efficient way to obtain H₂ plus CO₂ capture. Some figures are given in the study by Cormos [39]. The author made theoretical calculations by comparing different technologies for CO₂ capture during the H₂ production process at an industrial scale (300 MW_{th}) and using bioethanol as raw material. He concluded that the auto-thermal-chemical looping reforming (CLR) process exhibited highly energy efficiencies including 100% CO₂ capture.

The aim of this work is to give an overview of the options and the current status of the use of biofuels in chemical looping processes within the BECCS concept. The work has been organized considering the type of biofuel used in the CL process including gaseous, liquid and solid fuels. The opportunities and future trends of bio-CL are discussed considering the lessons learned during the use of different biofuels.

2. Biofuels and CO₂ capture

Biofuels currently represent one of the most important fuel sources to guarantee environmental and economic sustainability. They have emerged as both new energy resources and important alternatives for limiting greenhouse gas emissions.

Biofuels are considered a carbon neutral, renewable and abundant energy resource. They are considered neutral because CO₂ is removed from the atmosphere and stored by biomass formation through photosynthesis, to be emitted again into the atmosphere during bio-fuel combustion. Nevertheless, a carbon footprint can be attributed to the bioenergy concept when taking into account the life cycle of the production, transport, transformation and use of biomass. The carbon footprint is different depending on energy generation mix, and it would be lower as the energy system becomes renewable. This means that using biomass as fuel does not increase the total inventory of atmospheric CO₂ in significant figures. Nevertheless, when combined with CCS, the overall carbon footprint becomes negative [24].

Biofuels are generally classified as primary and secondary biofuels [40]. Primary biofuels are used in an unprocessed form, and mainly consist of woody biomass. In addition, different types of biomass coming from forestry and agriculture, as well as fishery products or municipal wastes, e.g. sewage sludge, or by-products and wastes originated from agro-industry or food industry, such as waste vegetable oil, can be considered. Secondary biofuels are derived from primary biofuels. Primary biofuels are treated by chemical, biological or thermal processes to yield a fuel with suitable characteristics for a determined use, e.g. ethanol, biodiesel, DME, etc. to be used in the transport or industrial sectors [41].

Biofuels can be also classified according to their physical characteristics. Biofuels can be solid, such as woody biomass; liquid, such as ethanol, biodiesel and pyrolysis oils; and gaseous, such as biogas, which is mainly composed of methane and CO₂, or gaseous compounds derived from biomass processing, such as pyrolysis gases obtained during biomass torrefaction or syngas from waste gasification. Gaseous and solid biofuels are normally used for heat and power production, whereas liquid biofuels are generally employed in the transport sector.

In this sense, a further classification also determines the type of CO₂ capture suitable for each biofuel. Thus, a brief description of each one of the biofuels is given in the subsection below. In addition, Table 2 summarizes the main advantages and disadvantages of using biofuels within the context of BECCS, which will later be explained in more detail.

2.1. Gaseous biofuels

The main gaseous biofuel is biogas. Biogas is generated by the anaerobic digestion of organic matter, including municipal solid waste, wastewater, animal manure and agricultural wastes [42]. Biogas production has experienced a great increase in recent years throughout the world, and this tendency is expected to continue in the near future [43, 44]. Global production of biogas in 2016 was 23 ktoe. The steady growth in the biogas sector has been particularly significant in Europe, with the number of biogas plants practically tripling in 6 years, with 17376 biogas plants and 459 biomethane plants in 2015, for a total installed capacity of about 9000 MWe. The total electricity produced from biogas accounts for 60.6 TWh, a number that corresponds approximately to the annual consumption of 13.9 million European households. Among the different countries in Europe, Germany stands out as the main contributor, followed by Italy and France. Biogas composition depends significantly on characteristics of the digested substrate and operating conditions. A typical biogas composition [42] is shown in Table 3.

Typical sour [45] and natural [46] gas compositions have also been included for comparison. Although natural gas composition depends on the reservoir from which it is extracted, it

contains different hydrocarbons, mainly methane and C_2-C_5 , with a minor presence of CO_2 , N_2 and H_2S . During well-head cleaning and processing, gas quality is improved to pipeline standards. In contrast, biogas presents a lower calorific value owing to the major presence of CO_2 coming from the fermentation process, and other minor impurities such as N_2 , O_2 , NH_3 and siloxanes.

The combustible components of biogas (mainly CH_4 , and some H_2 and CO) can be used as a fuel for transport or for heat/power generation despite the presence of non-combustible gases (mainly CO_2 and some N_2) greatly decreasing the heating value of the biogas [47]. However, the presence of different minor compounds prevents the safe use of raw biogas. Thus, siloxanes are converted into abrasive silicon dioxide particles during biogas combustion, which causes significant internal damage to engines or turbines. In addition, the highly corrosive hydrogen sulphide results in increased wear, frequent bearing damage and higher consumable costs. Therefore, the use of biogas currently involves important pre-treatment steps to remove these impurities (H_2S , NH_3 and siloxanes). Moreover, pre-treatment steps are required if the incorporation of biogas to the natural gas grid is desired.

In the development of CO_2 capture processes in the combustion of biogas, post-combustion processes are penalized by the high CO_2 content in biogas, although oxy-combustion could be an option. However, its high CO_2 content could be beneficial for H_2 production via dry steam reforming. In this way, CH_4 is converted into H_2 using the existing CO_2 in the biogas, although the effect of the presence of sulphur on the reformer catalyst should be taken into account.

It is also possible that some N_2 is present in landfill gas from air intrusion, which would penalize other CO_2 capture systems, such as oxy-combustion and chemical looping. In order to avert the presence of N_2 , air intrusion can be avoided by recycling CO_2 in a closed system [48].

Finally, other gaseous streams obtained from renewable sources can be considered as fuels in specific applications, such as the volatiles produced during biomass torrefaction and the syngas obtained during biomass or solid wastes gasification. In fact, biomass torrefaction has

been gaining in popularity in recent years as an alternative for increasing the energy density of biomass [49]. The volatiles produced, including both condensable and non-condensable ones, are burned with air in a combustion unit and the hot flue gases are used to provide the heat needed in the pre-drying and torrefaction stages.

2.2. Liquid biofuels

Unlike gaseous and solid fuels, liquid biofuels are predominantly used in the transport sector, which contributes as much as one third of total greenhouse gas emissions [5]. Therefore, liquid biofuels are being mainly investigated to replace conventional liquid fuels, namely diesel and petrol [40]. Secondary biofuels are being considered for this purpose, most commonly bioethanol and biodiesel. First generation bioliquids include products derived from sugars and starches, mostly by chemical or biological treatment. Second generation bioliquids follow the biomass-to-liquid (BtL) concept, with ethanol being produced from lignocellulosic biomass. In addition, dimethyl ether (DME) is being considered as a synthetic fuel produced from gasification processes, and it is easy to store and distribute. The algae-to-biofuel strategy is leading to the third and fourth generations of biofuels [40, 41].

Bioethanol represents the alternative renewable fuel with the largest potential to replace fossil-derived fuels, with world production of about 100 million m³ in 2015 [50]. Major producers of bio-ethanol are Brazil, from sugarcane juice and molasses; the United States, from corn starch feedstocks; and the European Union, from sugar beet. More than 20% of cars in Brazil are able to use 100% ethanol as fuel, including both ethanol-only engines and flex-fuel engines [50].

Global biodiesel production in 2014 was 528600 barrels per day, with the European Union being the largest producer with nearly half of all production [51]. The feedstocks to produce biodiesel depend on local availability. The dominant feedstocks in the European Union are

rapeseed oil, which accounted for 49% of biodiesel production in 2015, used cooking oil and palm oil.

In this sense, glycerol, as a by-product of biodiesel production, can be considered as an interesting biofuel contributing to the reduction of CO₂ emissions. In addition, there has recently been great interest in energy generation using primary bioliquids, such as waste vegetable oil, and other secondary bioliquids, such as pyrolysis pine oil.

The concern for CO₂ emissions and their impact on climate change has led to an increase in the production of renewable energy sources for use in transport. The use of liquid biofuels in mobile sources presents an interesting advantage with respect to fossil fuels, since this leads to neutral CO₂ emissions; see Fig. 3a.

Thus, the use of bio-ethanol in the transport sector can be considered almost neutral for the carbon balance in the atmosphere. However, CCS processes must be considered in order to achieve negative CO₂ emissions. In fact, H₂ from bio-ethanol with CCS can be used as an energy vector for the transport sector (see Fig. 3b) with two main advantages: (1) negative CO₂ emissions, and (2) the production of high purity bio-ethanol is not required. Note that the final dehydration step to produce anhydrous bioethanol represents important costs for the whole production process, which could be avoided with the above-mentioned H₂ production process [52].

The optimal use of liquid biofuels with CO₂ capture depends on the origin of the biofuel. For example, waste vegetable oil or glycerol can be suitable both for heat/electricity generation and H₂ production. In any case, CO₂ capture is acceptable in order to achieve negative CO₂ emissions. Nevertheless, the use of secondary fuels would be more convenient for H₂ generation with CO₂ capture once a large excess of this kind of fuel becomes available.

Steam reforming (SR), partial oxidation (POX) and auto-thermal reforming (ATR) are the most common processes for obtaining syngas/H₂ from bioethanol [53]. However, the incorporation

of CCS technologies into the use of renewable bioethanol fuel in the H₂ production process offers the possibility of achieving negative CO₂ emissions in the transport sector.

2.3. Solid biofuels

Among the different fuels, biomass has a long history as a major energy source, although nowadays the use of biomass in the energy mix is of minor relevance compared to that of fossil fuels. However, the use of biomass in bioenergy could be boosted in order to reduce dependency on fossil fuels. Therefore, the conventional thermochemical conversion approaches developed for fossil fuels, including combustion, gasification and pyrolysis, can now make use of biomass feedstocks. The general advantages and disadvantages of using biomass as a fuel are compiled in Table 2.

According to the *U.S. Billion-Ton Update* report, published in 2011, biomass is expected to replace 30% or more of American petroleum consumption by 2030 [54]. The European Union has outlined the National Renewable Energy Action Plan, which requires utilization of up to 40% biomass for electricity, heating and cooling by 2020 [55]. In addition, bioenergy integrated with carbon capture and storage (BECCS) is expected to make a significant contribution to the sustainability of the biomass energy supply, as pointed out by the IPCC in its Fifth Assessment Report [6] .

Considering mainly primary biofuels, such as woody biomass or agriculture residues, CO₂ capture in processes both for heat/electricity generation and H₂ production are of interest in order to achieve negative CO₂ emissions. In fact, the same CO₂ capture technologies used in coal-based combustion processes could be applied to biofuels. In the case of H₂ production, biomass gasification is a required step prior to CO₂ capture by pre-combustion processes.

Biomass gasification is viewed as one of the important and promising technologies because it offers the possibility to upgrade biomass to H₂, high value biofuels and other chemicals through bio-refinery process [56-58]. In order to obtain high quality syngas from biomass, a gasifying agent such as oxygen-enriched air is usually required instead of air during the

conventional biomass gasification process. N_2 dilution and the high cost of oxygen-enriched air production are included among the disadvantages of this process [59-61]. It should be also taken into account that this is a highly endothermic process where tars are also produced, reducing the gas yield and conversion efficiency while causing operational problems in the downstream equipment.

Some of these problems are solved by means of the fast internally circulating fluidized bed (FICFB) gasification process [62]. The basic idea behind the FICFB concept is to separate the gasification and the combustion zones, in order to obtain a largely nitrogen-free product gas. The system uses two interconnected reactors, the gasifier and the combustor, with a solid circulating between them. The endothermic gasification of the fuel is carried out with steam, and non-gasified fuel particles are transported with the bed material to the combustion reactor where it is burned with air to provide the heat required in the gasification reactor. The circulating solid acts as an energy vector, transferring heat from the combustor to the gasifier. However, CO_2 emissions are generated in the combustion reactor, and significant amounts of tar compounds are found in the product gas, which can be reduced by using catalytic filters downstream in the gasifier [63-65], or through the use of solids with some catalytic activity [66].

3. Chemical Looping process

The term chemical looping can include processes that transfer both CO_2 and O_2 . However, the former are usually referred to as calcium looping processes, whereas chemical looping typically refers to processes that transport oxygen. This work will focus only on those specific processes where a solid material acts as an oxygen carrier to transport the oxygen needed for the conversion of the fuel in a cyclic manner. The loop is completed when the depleted oxygen carrier is reoxidized with air before starting a new cycle. The main advantage of this process is that air and fuel are never mixed, and therefore the products of the fuel conversion are never

diluted with N₂ from air as they are in other conventional processes. In addition, a concentrated CO₂ stream is obtained at the outlet of the process.

Chemical looping technology is highly versatile, as it allows different combinations between fuels (gaseous, liquid and solids), processes (combustion, reforming, gasification, etc.) and final products (heat, electricity, syngas and H₂) [67, 68]. All these options include the possibility of CO₂ capture at a lower cost than state-of-the-art first-generation CO₂ capture processes. To date, the chemical looping concept has been successfully demonstrated for both gaseous, liquids and solid fuels, mainly fossil fuels [37, 67]. However, biofuels represent an interesting option for CL processes within the context of BECCS. The suitability of using these biofuels in chemical looping processes is discussed in this work. Fig. 4 shows the scheme of the main chemical looping processes, which include chemical looping combustion (CLC) and chemical looping with oxygen uncoupling (CLOU), chemical looping reforming (CLR) and chemical looping gasification (CLG), and chemical looping coupled with water splitting (CLWS).

In a CLC process, an oxygen carrier, a metal oxide (M_xO_y) normally transfers the necessary oxygen for combustion from the air to the fuel. The most common configuration is composed of two interconnected fluidized bed reactors, the fuel reactor (FR) and the air reactor (AR), with the oxygen carrier circulating between them [37, 67]. This system presents great similarities to conventional circulating fluidized bed boilers (CFBBs), which facilitates bridging the technology gap to commercial scale-up.

The oxygen carrier is reduced inside the fuel reactor, thus supplying oxygen to the fuel; see reaction R1. The reduced oxygen carrier is regenerated in the air reactor by taking oxygen from air; see reaction R2. The net chemical reaction taking into account both reactors is the same as that taking place in conventional air combustion; see reaction 3.

There are also specific oxygen carriers that have the ability to release gaseous oxygen [69]; see reaction R4. This ability is known as chemical looping with oxygen uncoupling (CLOU). In this case the fuel is burned with gaseous oxygen as it would be in a common combustion process with air (reaction R3).

If the purpose of the process is not combustion (CLC), but syngas/H₂ production (CLR), several reactions should also take place inside the fuel reactor. The process is referred as CLR for gaseous and liquid fuels and CLG for solid fuels. These reactions include the partial oxidation of the fuel (reaction R5), the reforming of the fuel (reaction R6) and the water-gas shift (reaction R7)

If the intended final product is H₂, the syngas passes through a water-gas shift (WGS) reactor, where water is added to increase hydrogen yield. Later steps include a CO₂ capture process (normally amines based) and pressure swing adsorption (PSA) for high purity hydrogen production. PSA-off gases can be reintroduced into the fuel reactor to increase exploitation of the fuel.

Finally, the CLWS process is based on the possibility of oxidizing some reduced metal oxides with water, producing H₂ as the end product. The fuel is burned in the fuel reactor as in a conventional CLC process. However, the reduced metal M_xO_{y-δ} is further reduced by H₂O to give pure H₂ after water condensing. The reduced oxygen carrier is then regenerated in the air reactor.

Obviously, the optimization of every reaction route for each specific chemical looping process depends on the oxygen carrier used, the configuration of the interconnected reactors, the type of reactor and the integration of the whole system. A more detailed description of these aspects can be found in the book by Prof. Fan [70].

3.1. Type of de reactors used in chemical looping

The chemical looping processes shown in Fig. 4 can be performed in different type of reactors and configurations, namely interconnected, moving or fluidized bed reactors and alternated packed or fluidized beds. Fig. 5 is a schematic of the different configurations.

Most of the CLC plants existing worldwide use the configuration based on two interconnected fluidized beds, one serving as the fuel reactor and the other as the air reactor. However, depending on the oxygen carrier reactivity, but mainly on the size of the CL unit, a wide range of different configurations has been used. At low scale, these includes the use of bubbling fluidized beds for both reactors [61, 71], an annular shape reactor with double circulating fluidized bed (CFB) loops [72], a spout-fluid bed instead of a bubbling bed for the fuel reactor [73], a series of three interconnected bubbling beds (one fuel reactor and two air reactors) [74], and two bubbling beds in series to improve volatiles conversion [75].

At higher scale, other alternatives to bubbling beds are preferred. The air reactor is normally a high velocity riser in order to provide the driving force for the solid material circulation. A dual circulating fluidized bed (DCFB) was used in the 120 kW_{th} unit for gaseous fuels at the Technical University of Vienna (TUV) [76], including a fuel reactor operating under a turbulent regime and connected with the air reactor through a hydraulic link. In contrast, the fuel reactor can be designed as a circulating CFB reactor, as in the case of the two largest CL installations currently in operation for solids fuels: 1 MW_{th} (TUD) [77] in Damsdtadt and 3 MW_{th} (Alstom Power USA) [78]. Based on the experience gained from these units, designs for a 100 MW_{th} unit [79] and a 1000 MW_{th} unit [35] have been developed. Both designs include the

configuration of two interconnected circulating fluidized beds, one for the fuel reactor and the other one for the air reactor.

The configuration of moving beds as fuel reactors has been also proposed at Ohio State University (OSU) [80]. The oxygen carrier is designed to flow counter-current to the gas, and the coal is fed into the system at an intermediate position in the reactor. This design allows volatile matter and gasification products to be converted inside the upper part while the char particles are gasified inside the bottom part. The design was further modified by Schwebel et al. [81] to facilitate fuel distribution inside the reactor. Although units up to 25 kW_{th} have been operated, the scale-up of the moving beds should be carefully evaluated, particularly with regard to the homogeneity of solids and temperatures across the section of the reactor. In any case, a fluidized bed connected to a riser is adopted for the air reactor. The use of an appropriate particle size valid for both for moving and fluidized beds is therefore a key aspect in this configuration.

The concept of moving beds has been widely used for the CLWS process, where both the fuel reactor and the steam reactor can operate under this configuration[70].

Chemical looping units operating at atmospheric pressure have so far been described. However, in order to achieve competitive energy efficiencies with respect to the power cycle burning gaseous fuels, operation at high temperatures and pressures (1-3 MPa) becomes necessary [82, 83]. In this sense, the use of dynamically operated packed-bed reactors has been proposed [84, 85], although the pressurized operation of interconnected fluidized beds is under development. The process consists of alternating oxidation and reduction reactions inside two separate reactors, using alternating periods of mild fluidization after each cycle to level off temperature and concentration profiles. The advantages to working under pressure depend on the use of an efficient gas switching system operating at high temperature and pressure. In addition, scale-up of the process would require careful control of the temperature

inside the reactors and a sophisticated system of valves to produce a continuous gas feed into the gas turbines.

More detailed information about the design and configuration of different chemical looping units can be found in the reviews by Adánez et al. [37, 67] and Fan [70]. In addition, the preferred configuration for each of the processes using biofuels will be described in the following sections.

3.2 Integration and dynamic analysis

The final use of a chemical looping process can be to produce energy (e.g. heat or electricity) and/or a value-added product (e.g. syngas or hydrogen). The design and operating conditions of the chemical looping unit will depend on the desired product, as well as the characteristics required for the oxygen carrier. In addition, the optimum integration of the chemical looping unit in the whole process also must consider its specific conditions.

For example, CLC can be used to produce process steam. This application seems to be one of the niches closest to the implementation of the process on an industrial scale. For good reason, the design of a 10 MW unit for the production of steam has been made for the purpose of producing steam for bitumen recovery from oil sands resources [86]. In this case, the required temperature of the reactors could be relatively low, e.g. 800 °C [87], and a highly reactive copper-based material can be a suitable oxygen carrier [88]. The integration of steam generation in the CLC process must consider the mass and enthalpy balance in the fuel and air reactors jointly. In the case of using a copper-based oxygen carrier with natural gas, both oxidation and reduction reactions are exothermic, although most of the heat will be generated inside the air reactor [67]. The heat generated during the fuel combustion would naturally be extracted from thermal energy in exhaust gases, both the depleted air from the air reactor and the concentrated CO₂ stream from the fuel reactor. But some heat must also be extracted from the solids circulating between the reactors [79]. The fraction of heat extracted from

solids varies depending on the solid circulation rate because the temperature of the reactors is closely related to this parameter. A mass balance defines the relationship between the solid circulation rate, the metal oxide content in the oxygen carrier and the variation of the solids conversion, which is shown in Fig. 6.

Thus, considering that a limit of $80 \text{ kg s}^{-1} \text{ m}^{-2}$ is imposed on the oxygen carrier circulation rate by fluid dynamic issues, an unequivocal relation between the suitable interval for the CuO content and variation of solids conversion can be calculated. These parameters are important for the enthalpy balance of the CLC unit, defining the difference of temperature between the air and fuel reactors; see Fig. 7a [89].

In addition, the integration between the fuel and air reactors affects the amount of solids required inside each reactor to achieve complete fuel combustion; see Fig. 8. taken from [90].

A direct effect of using interconnected reactors is that the required solids inventory increases as the variation in the solids conversion increases. Moreover, the solids inventory in the air or fuel reactor increases according to the intention for greater oxidation or reduction of the oxygen carrier, respectively. As a consequence, there is an optimum condition where a minimum amount of solids is required inside the entire CLC unit; see Fig. 8. Also, a dynamic simulation of the CLC must be performed in order to consider the optimum operating conditions during transitional periods [91].

The operating conditions of a CLC unit must be varied for the efficient generation of electricity. The use of a combined cycle, including steam and gas turbines, must be considered in order for the process to be competitive compared to a commercial natural gas combined cycle plant [92]. A pressurized CLC unit must be designed in order to supply hot and pressurized depleted air to the gas turbine. In addition, the efficient operation of a gas turbine requires gas temperature above $1200 \text{ }^{\circ}\text{C}$, with this being the required temperature for the CLC unit. Nickel-based oxygen carriers have shown the ability to operate at such high temperatures [93]. Considerations regarding solid circulation rate, metal oxide content and variation in solids

conversion are very similar to those shown by copper materials; see Fig. 7. However, the enthalpy balance differs from that of copper. With nickel, the reduction reaction is highly endothermic and, therefore, the fuel reactor temperature is lower than the air reactor temperature. Fig. 7b shows that the difference between the reactor temperatures depends on the NiO content and the variation in the solids conversion, which must be taken into account for the integration of the CLC unit into the whole energy generation process [89].

When syngas or hydrogen is the desired product, the process is based on the partial oxidation of the fuel, which can be gas or liquid in chemical looping reforming (CLR) or solid in chemical looping gasification (CLG). Of course, the product yield, whether syngas or hydrogen, is increased as the partial oxidation becomes less intense. But the degree of combustion should be high enough to support the chemical looping process under auto-thermal conditions, i.e. an external heat source should not be required. For example, by integrating pre-heaters and a water-gas shift reactor into a CLR system, auto-thermal conditions could be reached with an excess of 18% in the partial oxidation with regard to stoichiometric reaction R1 found in Ortiz et al. [94]. Under these conditions, 2.75 mol H₂/mol CH₄ could be produced, with excess heat recovered from the system for possible use in energy production or to meet steam/energy demands in a side process. This H₂ production is similar to the maximum H₂ yield that could be obtained in an auto-thermal reforming (ATR) process (2.8 mol H₂/mol CH₄), but with the advantage that an air separation unit is not required.

Hydrogen can also be produced by the chemical looping with water splitting (CLWS) method [95]. In this process, an oxygen carrier is highly reduced inside the fuel reactor. A partial oxidation is subsequently performed by steam to produce hydrogen followed by the complete regeneration of the oxygen carrier inside the air reactor. Iron oxide is typically used as the oxygen carrier material, which can be oxidized in air to Fe₂O₃, reduced to FeO or even Fe inside the fuel reactor, and partially oxidized to Fe₃O₄ inside the steam reactor. The integration of the three reactors must consider the thermochemical characteristics of the reduction of Fe₂O₃ and

the oxidation to Fe_3O_4 by steam. Thus, the fuel conversion to CO_2 and H_2O is limited by the thermochemical equilibrium when the iron oxide is reduced to FeO or Fe . For example, at 950°C , the equilibrium constant for the reduction with CO of Fe_3O_4 to FeO is $K_{\text{eq,Fe}_3\text{O}_4} = P_{\text{CO}_2}/P_{\text{CO}} = 2.3$, and that for the reduction of FeO to Fe is $K_{\text{eq,FeO}} = P_{\text{CO}_2}/P_{\text{CO}} = 0.42$. This means that the maximum CO conversion, limited by the thermochemical equilibrium, is 0.7 and 0.3 when Fe_3O_4 or FeO is reduced, respectively. In order to overcome thermodynamic limitations, a counter-current moving-bed reactor is proposed for the fuel reactor [95]. In this way, a high fraction of the oxygen present in Fe_2O_3 can be transferred, corresponding to an oxygen transport capacity of $R_{\text{OC}} = 30\%$. Of this whole amount of oxygen, 3.3% corresponds to the reduction of Fe_2O_3 to Fe_3O_4 ; 6.7% is for the reduction of Fe_3O_4 to FeO ; and the rest, i.e. 20%, is oxygen transferred by reducing FeO to Fe . However, the oxygen available for the reduction of Fe_3O_4 or FeO can be limited by the aforementioned thermochemical restrictions, thus restricting the conversion of the fuel before reacting with Fe_2O_3 inside the upper part of the moving-bed reactor. In this case, there must be enough oxygen available inside the upper part for the reduction of Fe_2O_3 to Fe_3O_4 in order to convert the fuel which could not be converted by thermochemical limitations. For example, if CO is considered the fuel, Fig. 9 shows the CO conversion as a function of the oxygen carrier-to-fuel ratio.

An oxygen carrier-to-fuel ratio equal to unity means that the flow of Fe_2O_3 from the air reactor has the stoichiometric oxygen to fully convert CO to CO_2 . But the oxygen carrier-to-fuel ratio must be above $\phi > 2.8$ in order to allow the complete conversion of CO to CO_2 in a counter-current moving-bed reactor. The oxygen carrier-to-fuel ratio also affects the temperature of solids at the reactor exit, which is lower than the inlet temperature of solids due to the endothermic reactions taking place inside the fuel reactor. This effect should be considered in the integration of the process because the reacting temperature also affects the equilibrium constants. The hydrogen produced depends on the amount of Fe and FeO to be oxidized to Fe_3O_4 in the steam reactor; see Fig. 9. For the case of $\phi = 2.8$, the hydrogen yield is 69% based

on the thermal conversion of CO to H₂. This value can be compared to the hydrogen yield of 83% for CLR.

3.3. Milestones in chemical looping

Chemical looping technology has experienced great development over the last 20 years. Table 4 summarizes the main milestones reached by chemical looping technology since the beginning of the concept. Although most of the milestones correspond to the use of fossil fuels, the experience gained could be also valid for the development of biofuel utilization. In this sense, the main events involving the use of biofuels in the different chemical looping processes have been also included in this table.

3.4. Chemical looping continuous units

The development of the chemical looping technology and the scale-up of the process are closely linked to the operation of continuous units. To date, chemical looping pilot plants in the range 0.3 kW_{th} to 3 MW_{th} exist worldwide for continuous operation with gaseous, liquid and solid fuels. Table 5 presents a summary of those continuous units including their location, power and reactor configuration. Most of the units were initially designed for use with fossil fuels. However, a number of them have been also tested with biofuels, as can be seen in the table. In addition, Figure 10 provides an overview of these continuous units distributed according to initial operation year, power and type of fuel used (gaseous, liquid and solid). Those units operating with biofuels have also been marked.

4. Chemical looping processes with biofuels

To date, the chemical looping concept has been successfully demonstrated for both gaseous and solid fuels, mainly coal [37, 67]. Biofuels are an alternative fuel for CL processes, the product of which can be heat/electricity or syngas. Figure 11 shows the chemical looping processes available for biofuels and the further use of the products obtained in these

processes. It should be highlighted that negative CO₂ emissions are only achieved where CO₂ is stored. Otherwise, neutral emissions are achieved.

Table 6 complements Figure 11 and provides a summary of the chemical looping processes involving the use of biofuels, which can be denominated as bio-CL, including the main features for each technology. The main division is produced between processes generating heat/electricity by combustion and those intended for syngas/H₂ production. A thorough description of the different bio-CL technologies can be found below. In addition, Table 7 gives a summary of the biofuels used in the different CL processes.

4.1. Biofuel combustion by chemical looping processes

If the desired product is heat or electricity, the process is based on the general concept of chemical looping combustion (CLC); see Fig. 4a. In this case, the oxygen required for complete fuel combustion in the fuel reactor is supplied by the oxygen carrier coming from the air reactor. In the CLC concept, CO₂ capture is inherent to the process, as air is never mixed with the fuel. Note that a highly pure CO₂ stream is obtained after cooling the product gas and H₂O condensation.

Among the combustion processes, biogas directly reacts with the oxygen carrier. Bioliquids require prior evaporation or decomposition to gaseous compounds, which can happen inside the fuel reactor without major difficulties. The direct use of solid biofuels can be handled through two different processes [37]: in-situ gasification integrated with chemical looping combustion (iG-CLC) and chemical looping with oxygen uncoupling (CLOU); see Fig. 12.

In iG-CLC, the solid biofuel, e.g. biomass, is gasified inside the reactor and the gaseous products react with the oxygen carrier. Thus, the fuel is dried, devolatilized and gasified by H₂O and/or CO₂, which are used as the fluidizing medium and gasifying agent; see Reactions (R10)-(R12). The molar ratio of the gasifying agent to fuel can be lower than that used in common gasification processes, as H₂O and CO₂ are already generated within the process after

combustion of volatile matter and gasification products with the oxygen carrier, M_xO_y ; see Reactions (R13)-(R15).

In CLOU, the oxygen carrier has the ability to release gaseous oxygen [69]; see Reaction (R4).

CuO and Mn_2O_3 are mainly considered among the metal oxides with suitable thermodynamic properties to release oxygen under conditions existing inside the fuel reactor. In this case, the gasification step is not a key stage for fuel conversion as the fuel is burned with O_2 in a way similar to that of common combustion with air; see Reactions (R16)-(R17).

In both cases, the oxygen carrier is regenerated in the air reactor by air; see Reaction (R18).

Considering the experience gained in CL processes using gaseous fuels [67], the possibility exists for transforming the biomass into a gaseous fuel by means of prior gasification/pyrolysis processes. Thus, the syngas-CLC and pyrolysis gases-CLC require previous steps involving pure O_2 or N_2 , respectively. In the case of syngas-CLC, CO_2 capture is achieved in the CLC unit owing to the use of pure oxygen for the biomass gasification, avoiding dilution with N_2 in the syngas produced. In the pyrolysis gases-CLC process, CO_2 capture is related to the carbon in the charcoal produced, which can be deposited in soils [170, 171]. Carbon in pyrolysis gases can be

also captured by CLC, but in this case, the use of N_2 during pyrolysis would not be recommended.

4.2. Production of syngas/ H_2 from biofuels by chemical looping processes

To produce syngas, the oxygen supplied by the oxygen carrier must be below the stoichiometric amount required to achieve complete combustion of the biofuel. In this case, partial oxidation of the fuel is required to produce syngas; see Fig. 4b. The degree of partial oxidation must be high enough in order to maintain the endothermic reforming or gasification reactions, thus achieving an auto-thermal process [52, 94]. The main advantage of the use of a CL process for syngas production is that syngas is not diluted in N_2 ; therefore, a syngas with high heating value is obtained without the use of pure O_2 . The product gas is a mixture of H_2 and CO as major components, H_2O and CO_2 as by-products of the partial oxidation, and minor products as unconverted or intermediate compounds, such as CH_4 or tar. In the case where H_2 is the desired product, the H_2 yield must be maximized via a water-gas shift reaction, and then a pre-combustion CO_2 capture step is needed in order to separate the H_2 from CO_2 . The intrinsic advantage of using chemical looping processes is that a non-diluted mixture of H_2 and CO_2 is achieved by an auto-thermal process. In addition, there is the possibility for producing a pure N_2 stream inside the air reactor [52, 172], potentially for ammonia or urea synthesis.

In the case of biogas and bioliquids in chemical looping reforming (CLR), the fuel must be partially oxidized, but reforming reactions are also required to maximize the conversion of the fuel to syngas components, namely H_2 and CO. Thus, catalytic activity of the oxygen carrier for reforming reactions is a key issue in the CLR process. The possibility for obtaining different H_2/CO molar ratios under auto-thermal CLR conditions is particularly interesting, as these can be adjusted depending on the use of the syngas produced, as has been demonstrated with non-renewable fuels, e.g. synthetic fuels by the Fischer-Tropsch process [173].

When a solid fuel is considered, the fuel must be gasified in-situ, in what is referred to as the chemical looping gasification (CLG) process. CLG considers the gasification of the solid fuel by

partial oxidation to produce H_2 and CO as product gas without the use of an air separation unit (ASU). Thus, this process takes advantage of the CLR concept, but a solid fuel is used instead of methane. In addition, experience gained in the CLC process with coal is of great value for the development of CLG with biofuels, such as biomass [37].

CLG has the potential to prevent any CO_2 emissions and reduce the amount of tar in the product gas. In fact, biomass chemical looping gasification (BCLG) is an emerging technology that shows good potential for efficient biomass gasification by eliminating the need for energy-intensive gas separations in order to achieve a non-nitrogen diluted syngas stream. BCLG involves the use of an oxygen carrier (OC) to transfer oxygen from air to the biomass to convert the biomass into syngas while the traditional gasifying agents, such as oxygen or enriched air, are avoided.

BCLG shares similar principles with CLC, as illustrated in Fig. 12c, and the reactions involved are the same, although the level of completion is different in both cases. In BCLG, biomass is partially oxidized to produce syngas (mainly, $CO+H_2$) as opposed to being fully oxidized in CLC, where the desired product is heat and electricity. In BCLG technology, lattice oxygen from the oxygen carrier is used to replace pure gaseous oxygen in order to gasify the fuel. Biomass is pyrolysed into gas (pyrolysis gas), liquid (tar) and solid (char) inside the fuel reactor, and then the products of pyrolysis react with the oxygen carrier. Also, steam reforming of gasification products, such as CH_4 or tar, assisted by the presence of an oxygen carrier can contribute to the H_2 yield [133]. Thus, solid fuel is converted to syngas and the oxygen carrier is reduced in parallel. The reduced oxygen carrier is regenerated inside the air reactor in an air atmosphere in order to begin a new cycle.

In comparison with other biomass gasification technologies, BCLG has several potential advantages, which are as follows:

- (i) OC reduction by biomass in the fuel reactor is a strongly endothermic process, while the oxidation of the reduced OC by air in the air reactor is an intensively exothermic process.

Thus, the heat for endothermic biomass gasification and reduction reactions in the fuel-reactor is provided by the oxygen carrier coming from the air reactor to the fuel reactor at high temperatures. No carbon combustion is used to provide heat to the process, therefore preventing CO₂ emissions. The energy balance is guaranteed due to the partial combustion carried out in the fuel reactor, and no other external heat source is required.

(ii) The recycling of the oxygen carrier provides lattice oxygen for biomass gasification, saving on the cost of pure oxygen production or large amounts of steam. Air separation unit (ASU) is avoided.

(iii) Syngas is not diluted with N₂.

(iv) The OC particles can also act as catalysts for the decomposition or reforming of the tar, which are undesirable products in biomass gasification, in order to produce clean syngas.

The compilation of all these advantages clearly shows that BCLG allows the conversion of biomass into high-quality syngas with an appropriate H₂:CO ratio in a single step without the use of molecular oxygen and capital-intensive units, including a tar reformer and air separation units. Such high-quality syngas generation would allow downstream processing to produce H₂ (via water-gas shift, WGS), or biofuel and chemicals (via Fischer-Tropsch, FT), reducing both capital and operating costs.

However, unlike the iG-CLC process, the fuel reactor in CLG is operated at high concentrations of H₂ and CO. The presence of the oxygen carrier in iG-CLC promotes in-situ gasification through the rapid consumption of gasification inhibitors, i.e. H₂ and CO. In comparison with iG-CLC, the slower gasification rate of CLG requires the residence time of solids in the fuel reactor to be increased.

Chemical looping technology can also be used to reduce the tar content in the gasification products of biomass [174-176]. For this purpose, a selective oxygen carrier must be designed to convert the volatile organic compounds and tar, although the degree of combustion must

be maintained at a low level in order to prevent a significant decrease in the heating value of the syngas.

Finally, the potential of some compounds to be oxidized by steam can be exploited for hydrogen production in a chemical looping unit; see Fig. 4c. In this case, the oxidation step that takes place inside the air reactor of the chemical looping combustion unit is partially replaced by oxidation with steam, which gives hydrogen as a product. In this process, high-purity hydrogen can be obtained after condensation of the unreacted steam. Thus, hydrogen generation is based on the water splitting reaction, a process referred to as chemical looping coupled with water splitting (CLWS) [177].

The CLWS process takes advantage of the equilibrium formed between steam and a reduced form of a metal oxide, mainly iron oxide, although other materials such as spinels can be also used [178]. For example, metallic iron (Fe) or wüstite (FeO) can be oxidized in a steam reactor to magnetite (Fe₃O₄) producing H₂:

A further complete oxidation to haematite (Fe₂O₃) is achieved by oxidation in air:

Subsequently, the iron oxide is completely reduced in the fuel reactor; see Reactions (R20)-(R24). The solid fuel undergoes previous drying, devolatilization and gasification, according to Reactions (R10)-(R12).

The fuel reactor design must allow complete combustion of fuel to CO_2 and H_2O . If a reactor is designed for the perfect mixing of solids, reduction to FeO or Fe will not allow complete conversion of fuel to CO_2 and H_2O . Instead, a counter-current moving bed for the fuel reactor has been proposed [95]. In the moving bed configuration, a staged reduction is expected as the oxygen carrier descends. First, reduction of Fe_2O_3 to Fe_3O_4 can take place in the upper part, allowing complete combustion of the fuel to CO_2 and H_2O . Below this is where the reduction of Fe_3O_4 to FeO or even Fe , which are the important compounds for H_2 generation in the steam reactor, happens.

This concept is suitable for hydrogen and power co-generation [179, 180]. There is flexibility in the fraction of energy produced as hydrogen or power, as different degrees of reduction to FeO or Fe can be achieved, which results in different H_2 yields. The energy penalty in the CO_2 capture is lower than that of other benchmark technologies, at only 3.5%, while a high energy efficiency of 42 % is estimated [181].

By fixing the air flow to the stoichiometric amount, a nitrogen stream can be obtained from the air reactor [172], which can be used for ammonia or urea synthesis, together with the H_2 produced in the same CLWS process [182, 183].

5. Considerations on the use of biofuels in chemical looping processes

5.1. Biogas

The first developments in chemical looping technology in early 2000s were accomplished using gaseous fuels. The technology has since experienced a great advance with the use of different fossil fuels, including natural gas, syngas and refinery gas, among others, as well as with the use of a wide variety of synthetic oxygen carriers. Gas-fuelled CL technology has been satisfactorily tested at the 120-140 kW scale both for combustion and reforming processes [67, 109, 118]. However, the use of biogas in a chemical looping process introduces new challenges and opportunities.

The main differences between natural gas and biogas refer to their composition, see Table 3. The presence of H_2S and CO_2 do not present any differences because there is wide experience in cleaning and separation processes. However, the presence of siloxanes and nitrogen in biogas could be considered the more specific challenges. A further description of the biogas use taking these characteristics into account can be found below.

5.1.1. Combustion for heat/electricity production

The use of biogas in chemical looping combustion (CLC) could solve some of the issues regarding the pre-treatment or cleaning steps currently necessary in conventional combustion processes while producing the same heat. In fact, it is not necessary to upgrade the biogas stream (i.e. separate the CO_2) since the CO_2 can easily be handled in a CLC process.

Experience in biogas-fuelled CLC is scarce. Hoteit et al. [184] analysed the feasibility of biogas combustion and reforming using nickel and copper-iron oxygen carriers ($NiAl_{0.44}O_{1.67}$ and $Cu_{0.95}Fe_{1.05}AlO_4$) in a batch fluidized bed. They evaluated the effect of bed temperature, solids inventory and superficial gas velocity in the course of several reduction/oxidation cycles by using a synthetic biogas to simulate the composition of a French landfill (46%vol CH_4 , 31%vol CO_2 , 3%vol O_2 , and 20%vol N_2).

If the intention is to achieve high combustion efficiencies, the oxygen carrier used should be not only be highly reactive with respect to CH_4 but also sulphur resistant, given the sulphur content in biogas. Previous experience in continuous CLC units showed that this is possible when CH_4 was burned in presence of high H_2S concentration with Fe-based oxygen carriers prepared by impregnation [112, 185].

Moreover, biogas can contain some N_2 . In this case, N_2 will exit together with CO_2 in the fuel reactor flue gas. The need for N_2 separation would depend on the CO_2 transport and storage standards to be met. Physical absorption could be an efficient and economical option after combustion due to high partial pressure of CO_2 . The removal of N_2 from the biogas prior to its combustion in a chemical looping combustion reactor could be another option.

In addition to biogas, other gaseous fuels coming from biomass processing have been considered for combustion in a CLC process. Sarvaramini and Larachi [186] tested the behaviour of an Fe-based oxygen carrier in order to evaluate the integration of the heat generated during the combustion of torrefaction volatiles into the overall process, including CO₂ capture. Moreover, Huang et al. [187] investigated the performance as oxygen carriers of several Cu, Ni and Fe oxides supported on ceria during the chemical looping combustion of biomass-derived syngas at laboratory scale. No testing of biogas combustion in continuous CLC units has been reported to date. However, the wide experience existing regarding the use of natural gas guarantees the possibility for using biogas without major drawbacks.

5.1.2. Syngas/H₂ production

Considering the presence of CO₂ in biogas, another possibility is the use of the chemical looping dry reforming (CLDR) process as a means of biogas valorization [188]. The syngas obtained could be further used for the Fisher–Tropsch synthesis of fuels or chemicals. The authors conducted cyclic reduction and oxidation tests using a Ni/CeO₂ oxygen carrier in a fixed bed quartz reactor. The use of this CLDR overcomes the drawbacks of conventional dry reforming of methane (DRM) such as the high temperature needed to produce the endothermic reaction (external heat is needed). High temperature causes the sintering of the catalysts, coke formation and catalyst deactivation. Obviously, the use of Ni-based oxygen carriers in these processes make necessary the use of sulphur-free biogas, making the implementation of prior cleaning steps necessary.

Lima da Silva et al. [189] carried out a thermodynamic study for a proton exchange membrane fuel cell (PEMFC) system integrated with a biogas chemical looping reforming processor, and compared this option with other biogas reforming technologies, namely steam reforming (SR), partial oxidation (PO) and auto-thermal reforming (ATR). They obtained a high hydrogen yield (2.6 mol per mol of CH₄) in an auto-thermal process and pointed out the economic benefits of the CO₂ capture in a carbon market, considering the high CO₂ present in the biogas.

In addition, CLR can be used as a secondary tar-cleaning process for upgrading biomass-derived gas [174-176, 190-199]. The idea behind the tar-cleaning method is to reform tar components (C_nH_m) into useful gas molecules. The gas composition of the inlet stream and its tar content vary somewhat depending on gasifier operation.

Several studies analysed the use of the raw gas obtained from 2-4 MW indirect gasifier at the Chalmers University of Technology. The tests were carried out in a continuous bench-scale CLR reactor at temperatures between 750 and 880 °C. Bed materials tested included ilmenite [196, 198, 199], catalysts based on nickel [176] and manganese [175], and mixtures of ilmenite and NiO/Al_2O_3 [197]. The main parameters to consider in the process were the efficiency of tar reforming in the fuel reactor, by analysing the tar content at the inlet and outlet streams, and regeneration after coke formation, by measuring the CO and CO₂ concentrations at the air reactor outlet. Tar removal efficiency in the range of 60-95% were obtained at temperatures above 850 °C. In addition, no deactivation of the materials was observed in any case due to coke accumulation during the regeneration cycles.

Other works at laboratory scale includes the possible use of materials based on Fe [174], Cu and La, Sr and Fe [192, 193, 195].

5.1.3. Opportunities for biogas-fuelled chemical looping processes

Although the use of biogas in chemical looping processes has been only tested at laboratory scale, the implementation of the technology can be based on the wide experience gained from the gaseous-fuelled chemical looping process. This type of fuel was the first to be used in both CLC for heat and electricity production and CLR for syngas/H₂ production [67]. This broad experience includes:

- About 3300 hours of operational experience in continuous units.
- A great variety of fuels including natural gas, syngas, refinery gas, sour and acid gas, etc.
- A great variety of oxygen carriers based on Ni, Fe, Cu, etc. Synthetic oxygen carriers are preferred to achieve complete fuel conversion.

Therefore, there are very many development opportunities for the dual use of biogas in chemical looping processes. On the one hand, considering the dispersion and scale of biogas production plants, small CLC units should be suitable for heat production. The CO₂ captured could be used for different purposes, although the scale of its use in CCU processes is too small and storage times too short to become significant as a means of mitigating climate change [25]. Therefore, neutral CO₂ emissions would be produced instead of negative ones; see Fig. 2. The most suitable configuration would be two interconnected fluidized bed reactors using synthetic oxygen carriers based on copper or iron. In both cases, it would be necessary to include a desulphurization step prior to or after combustion.

On other hand, the composition of the biogas is valid for the use of the CLDR process for syngas production. In addition, tunable H₂/CO ratios can be achieved by adding steam to the fuel mixture. Given the advantages of the catalytic materials, Ni-based oxygen carriers would be desirable in CLDR, although a prior cleaning step would be required. In any case, negative emissions would be achieved only in the case where the final product is hydrogen, together with CO₂ capture and storage.

In relation to the presence of siloxanes, this pollutant should not affect combustion in CLC since SiO₂ is one of the most commonly used materials used in fluidized beds. However, the effect of the siloxanes/SiO₂ on oxygen carrier reactivity should be experimentally tested. In summary, the possibility of using raw biogas is a great opportunity for chemical looping technologies, which could reduce the cost associated with gas cleaning steps. In this sense, the existence of sulphur-resistant oxygen carriers is of great significance [112, 185].

In addition to biogas, other gaseous fuels coming from biomass processing also present interesting options, such as the use of volatiles obtained during torrefaction or biomass-derived syngas in CLC and the use of CLR as a secondary tar-cleaning process.

5.2. Liquid biofuels

In contrast to gaseous and solid fuels, the use of liquid fuels in chemical looping processes has experienced a lesser degree of development. Most of the experience gained with liquid fuels in CL processes is related to the use of fossil fuels [122, 125, 173, 200-202]; however, additional advantages can be obtained if the liquid fuel comes from renewable sources.

5.2.1. Combustion for heat/electricity production

There is relatively little experience in the use of bioethanol in the CLC process in continuous units. Most of this experience corresponds to the work by de Diego et al. [124], who presented the experimental results obtained in a 1 kW_{th} CLC unit burning ethanol for more than 100 hours of continuous operation. The authors demonstrated the viability of using ethanol in the CLC process and of different oxygen carriers prepared by impregnation on γ -Al₂O₃ and α -Al₂O₃: Cu14- γ Al, Fe20- γ Al, Ni21- γ Al and Ni18- α Al. The suitability of the use of the oxygen carriers was finally decided taking into account oxygen transport capacity and hydrodynamic criteria. Additional tests carried out in the CLC unit feeding ethanol and water, simulating bioethanol with different purities, did not show any effect of water on either combustion efficiency or the CO₂ capture process, although this will negatively affect the energy balance of the entire system.

5.2.2. Syngas/H₂ production

Several works can be found in the literature on the use of bioethanol in CLR processes. Most of them correspond to discontinuous tests carried out at laboratory scale for the development or testing of new materials as oxygen carriers and to analyse the effect of operating conditions, including pressure [203-208].

In contrast, García-Labiano et al. [123] and García-Díez et al. [173, 200] reported more than 100 hours of continuous operation in a 1 kW_{th} continuous CLR unit using ethanol as fuel and two Ni-based oxygen carriers, NiO21- γ Al₂O₃ and NiO18- α Al₂O₃. These authors experimentally demonstrated the viability of the CLR process with perfect control of the oxygen reacted in the fuel reactor for syngas production. Moreover, a pure N₂ stream was obtained at the outlet of

the air reactor. In addition, it has to be considered that the bioethanol production process for use as liquid fuel in motor vehicles requires intensive distillation and dehydration processes to remove the water and obtain a high purity fuel. These purification steps represent about 37% of the total energy needed in the whole process. However, if we consider the use of the energy vector H_2 as the required fuel for cars obtained through a CLR process, including carbon capture and storage, the use of a diluted bioethanol stream could be an interesting option. In fact, García-Díez et al. [52] conducted a theoretical study on the possibility of using different bioethanol purities in a H_2 production plant with an auto-thermal CLR process. The grades considered were dehydrated (~100 vol%), hydrated (~95.2 vol%) and diluted (~52 vol%) bioethanol. They concluded that it is possible to produce the same hydrogen production values, about 4.4 mol of H_2 per mol of ethanol at auto-thermal conditions for different bioethanol purities; see Fig. 13.

This was a remarkable result considering the significant energy and cost savings that could be achieved in the bioethanol production process through the removal of the final dehydration step.

Other liquid fuels have been also tested at laboratory scale for syngas production through the CLR process. These include waste cooking oil [209], glycerol [210, 211], pine pyrolysis oil and palm empty fruit bunches oil [212], and mixtures of ethanol and the aqueous fraction of pine pyrolysis oil [213].

With regard to the type of oxygen carrier to be used in CLR, all the above-mentioned works use materials based on nickel owing to the catalytic effect of metallic Ni on the fuel reforming reaction. The addition of a solid sorbent together with the oxygen carrier with catalytic properties to selectively remove the CO_2 could enhance hydrogen production through the sorption-enhanced reaction process (SE-CLR). The sorption-enhanced process has been widely studied in the past for steam methane reforming. The process has now been extended to the use of several liquid biofuels such as glycerol [214-216] and waste cooking oil [217]. Several

calcium-based sorbents, including limestone and dolomite, have been tested in their calcined state for CO₂ removal. Hydrogen purity exceeding 90% was found at the optimum conditions: temperatures about 500–600 °C during reforming and about 900 °C during regeneration. No decay in the activity of the materials was observed, although further studies, including the use of more redox cycles, are required.

5.2.3. Opportunities for bioliquids in chemical looping processes

Although technically possible, the combustion of bioethanol, or even biodiesel, in CLC boilers to produce heat and/or electricity is not economically viable. Both bioethanol and biodiesel are secondary fuels, and the combustion process could be carried out more economically if they were primary fuels.

Nevertheless, the use of other related liquid fuels could be seen as potential feedstocks for chemical looping processes. In fact, rising biodiesel production from vegetable or animal feedstocks in the near future will lead to an increase in the glycerol side-product. It should be taken into consideration that 10 kilograms of crude glycerol is produced for every 100 kilograms of biodiesel. In fact, glycerol is an ideal fuel for combined heat and power installations as it is non-toxic, non-odorous, non-volatile, water soluble and non-flammable. Its use in the CLC process with CO₂ storage can contribute to achieving negative CO₂ emissions. Similar considerations can be made for the use of dimethyl ether (DME), which is often considered a clean synthetic fuel that is easy to store and transport.

However, all of these kinds of fuels are highly recommended for H₂ production with CCS in order to decarbonize the transport sector. The use of bioethanol can be of interest, especially in countries with a surplus of this biofuel, such as Brazil [218, 219]. In this case, negative CO₂ emissions can be considered if CO₂ is captured and sequestered, because carbon from biomass is neutral in the CO₂ cycle. Other liquid fuels with good perspectives are waste cooking oil and biomass pyrolysis oils.

The configuration of two interconnected fluidized bed reactors would be the most suitable configuration for the use of liquid biofuels. However, in order to avoid excessive expansion of the bed due to gas generation during liquid processing inside the fuel reactor, CO₂ recirculation from the outlet stream could be advantageous to produce a more homogeneous gas velocity inside the reactor [220]. With regard to suitable oxygen carriers, any material based on Cu, Fe, or even CLOU materials will be suitable for CLC. In contrast, Ni-based oxygen carriers with catalytic activity will be preferable for CLR. The low or zero sulphur content of biofuels presents a great advantage with respect to fossil fuels because no deactivation of the oxygen carrier would be expected.

5.3. Solid biofuels

Chemical looping processes (CLPs) have great potential for both the combustion and gasification of solid fuels, such as coal and biomass. Chemical looping processes developed for coal combustion or gasification are being adapted to the combustion of biomass [37]. Thus, the combustion of biomass in chemical looping can be performed via in-situ gasification (iG-CLC) or oxygen uncoupling (CLOU) mechanisms. In this case, heat is the product, which can be used for electricity or steam generation. Hydrogen can be obtained as a profitable product by performing the gasification via a partial oxidation of biomass (CLG) or by taking advantage of the water splitting process (CLWS).

5.3.1. Combustion of biomass by iG-CLC and CLOU processes

Combustion is the most common method for obtaining heat from biomass. Reactor designs in conventional burners include fixed beds, suspension burners, fluidized bed combustion systems, etc. The main products of efficient biomass combustion are carbon dioxide and water vapour, although tar, smoke and alkaline ash particles are also produced. In any case, the use of biomass in conventional boilers leads to almost neutral CO₂ emissions.

The combustion of biomass in chemical looping processes introduce several advantages, including the possibility for achieving a negative CO₂ balance, higher thermal efficiency and reduction in NO_x formation [221]. In addition, there is lower corrosion in heat exchangers because heat in CLC systems is extracted in the air reactor, where no alkaline components are present.

There is currently wide experience on CLC using coal as fuel. However, the different characteristics and properties of biomass compared to coal introduce new challenges for the CLC process. Recently, Salimbel and Beal [221] conducted research to assess how the different properties of biomass influence CLC performance as compared to coal. The higher amount of volatile matter in and the char reactivity of biomass generally produce an increase in both CO₂ capture efficiency and oxygen demand. The higher alkaline content in ashes and the interaction with the oxygen carriers should be also considered.

The combustion characteristics of several types of biomass (rice hulls and husks, sewage sludge, wood char and pine sawdust) have been determined at laboratory scale in a thermogravimetric apparatus (TGA), fixed bed and bench moving bed. The oxygen carriers tested include the use of NiO, CuO, manganese ores and Fe₂O₃. CLOU materials have been also tested: Cu-based, and several mixed oxides including Cu-Mn, Mn-Fe, Mn-Si-Ti [222-230]. In addition, tests have been carried out in continuous units at different scales ranging from 0.5 kW_{th} to 4 MW_{th}. Pine sawdust and wood chips are the most usual types of biomass used in these continuous units, although sewage sludge, wood char, olive stones and almond shells have also been used. Table 8 shows a summary of the works related to the use of solid biofuels in continuous units, including the main operating parameters and results.

Most of tests were carried out under iG-CLC mode using H₂O as gasifying agent. The preferred oxygen carriers were those based on Fe, including both iron ore [73, 231-235, 238, 239] and ilmenite [160, 168, 237], and manganese ores [168, 236]. However, the high reactivity exhibited by the synthetic copper-based oxygen carriers made them highly suitable materials

for biomass combustion, where their high volatile content resembled that of gaseous fuels [241]. It should be highlighted that CO₂ may be used instead of H₂O as a fluidizing gas for biomass, with important energy saving associated with steam generation [73, 231].

The possibility of achieving negative CO₂ emissions using biomass in a CLC process has been demonstrated in several laboratory-scale units. In fact, 100 % CO₂ capture efficiency was reached at Instituto de Carboquímica (ICB-CSIC) with several types of biomass (pine, almond shells and olive stones) [232], at Southeast University (SU) using sawdust and sewage sludge [233, 234], etc. The high reactivity of biomass char particles allows these results to be obtained even without the need to use a carbon stripper.

However, the difficulty in burning all the volatile matter in the fuel reactor often produces high oxygen demand values in the process [231, 232]. Oxygen demand is particularly high when non-optimized conditions are used in the fuel reactor. For example, high oxygen demand values were found in a 4 MW_{th} unit where the fuel reactor was a bubbling fluidized bed and the biomass was fed onto the surface of the bed [168]; high oxygen demand values were also identified in a 1 MW_{th} unit due to the low solids inventory existing in the fuel reactor [239]. High oxygen demand values imply that combustion must be completed with an oxygen polishing step downstream of the fuel reactor using pure oxygen, in order to obtain a pure CO₂ stream ready for transport and storage. In contrast, the small amount of tar present in the combustion gases at the fuel reactor outlet does not present any problems for the oxygen polishing step [231]. The CLOU mode has been evaluated at a lower scale in comparison with iG-CLC, although this process presents important advantages over iG-CLC. Table 9 shows the CLOU materials tested at laboratory scale.

In contrast, biomass combustion tests in CLOU mode were carried out in continuous units with oxygen carriers based on Cu [131], Cu-Mn oxides [240] and calcium manganate which have oxygen uncoupling capabilities at temperatures of interest [151]. These materials were able to completely burn the solid biomass producing almost pure CO₂ streams. Small amounts of

oxygen could be found together with the CO₂ at the fuel reactor outlet due to the gaseous oxygen released by the oxygen carrier.

A comparison between the iG-CLC and CLOU processes can be made using the results obtained in the same continuous unit and using the same types of biomass (pine sawdust, olive stones and almond shells) [231, 232, 240, 242]. Fig. 14 provides a comparison of the CO₂ capture efficiency and combustion efficiency obtained in both iG-CLC and CLOU modes at ICB-CSIC for different biomasses in a 1.5 kW_{th} continuous unit without a carbon stripper.

CO₂ capture efficiency represents the percentage of the carbon introduced with the solid fuel that is captured in gaseous form at the fuel reactor outlet. In contrast, combustion efficiency is a measure of gas conversion inside the fuel reactor, including both volatile matter and gasification products.

On one hand, very high CO₂ capture values were achieved by optimizing the fuel reactor temperature in both combustion modes. In fact, 100% CO₂ capture efficiency was obtained in iG-CLC mode at temperatures above 950-975 °C with the three forms of biomass. However, a temperature above 930 °C was required in CLOU mode. This temperature could be achieved with a Cu-based material; but the operating temperature for a Cu-Mn mixed oxide was limited below 850 °C to avoid de-fluidization problems and to allow a suitable temperature in the air reactor to regenerate the material. Under these conditions, maximum CO₂ capture rates of 90-95% were obtained. In any case, the use of a carbon stripper between the fuel and air reactors would increase CO₂ capture efficiency in CLOU mode [37]. On the other hand, combustion efficiencies of about 70-80 % were obtained in the iG-CLC, which makes it necessary to incorporate an oxygen polishing step downstream of the fuel reactor in order to obtain a pure CO₂ stream. However, full combustion efficiencies were obtained at all temperatures in CLOU mode, which is a very important advantage of this combustion process. These good results are the consequence of the improved reaction rate between the volatile matter and gaseous oxygen produced by the CLOU particles in the fuel reactor. This is possible because these CLOU

particles are able to produce at least the amount of gaseous oxygen required and at a fast enough rate to burn the volatile matter. Obviously, every type of CLOU particle has to be used within a feasible temperature interval: 750-850 °C for the Cu-Mn based materials, and 900-950 °C for those based on Cu. This temperature range is given for the oxygen concentration in equilibrium for each type of material [243].

During the initial development of the CLOU process, the poor durability of the oxygen carrier particles was a weakness for the scale-up of the process. A low lifetime was found for particles based on CuO supported on MgAl_2O_4 [244]. However, the use of Cu-Mn mixed oxides under suitable operating conditions showed that the durability of the particles could be significantly improved [245]. Suitable operating conditions depend on a high solid circulation rate in order to avoid high oxygen carrier conversion through the fuel reactor. In addition, these conditions are also optimal for maximizing CO_2 capture efficiency.

In summary, although recent advances predict a high potential for bio-CLC, there are still important challenges to overcome. Among them are the lifetime of oxygen carriers (especially CLOU materials), the interaction between oxygen carriers and biomass ashes during long exposure times, and the improvement of the CLC design in order to reduce high oxygen demands in CLC during biomass processing.

A new process known as oxygen carrier-aided combustion (OCAC) has recently been used to test oxygen carriers at important scale, although it is not strictly a CLC process since it does not include CO_2 capture in the system. OCAC refers to the process where an oxygen carrier instead of an inert solid is used as bed material during combustion in a fluidized bed boiler [246, 247]. In this process, the active oxygen carrier is reduced inside fuel rich parts of the boiler and oxidized into oxygen rich locations. In fact, promising results were found during combustion of wood chips as fuel in the 12 MW_{th} CFB boiler at Chalmers University (CUT) with ilmenite or manganese ore as bed material [248-251], as well as during combustion of municipal solid waste in an industrial 75 MW_{th} FBC [252].

Nevertheless, some aspects must be considered in order to extrapolate oxygen carrier behaviour from OCAC to CLC. For example, interaction with ash and the extent of the oxygen carrier reaction may be different, which would affect particle ageing [249]. Although Na deposition on the iron ore-based oxygen carrier particles does not seem to pose a problem [253], the interaction of alkaline compounds with Mn-based oxygen carriers should be further investigated.

Finally, several measures have already been undertaken or proposed to minimize the unburnt compounds in iG-CLC units, including options to improve gas-oxygen carrier contact or incorporate new design concepts into the current scheme of the iG-CLC system. Fig. 15 shows the preferred configurations for the improvement of the iG-CLC process using biomass.

The immersion of a volatile distributor inside the fuel reactor has been proposed by Lyngfelt and Leckner [35] to promote the contact between the oxygen carrier particles and the volatile matter. Thus, the conversion of volatile matter is expected to be increased. Other alternatives to improve the gas conversion are the use of a secondary fuel reactor, which would be fed by gases exiting the primary fuel reactor, or to recirculate the gases to the fuel reactor in order to improve their combustion [254].

5.3.2. Syngas/H₂ production by the Chemical Looping Gasification process

BCLG technology is a new and promising technology for syngas production that has recently been developed. The first works at laboratory scale appeared in 2013, and the efforts for the development of this technology have been increasing since then, particularly in China. There are laboratory-scale works, mainly based on thermogravimetric data or batch fluidized beds, analysing the use of different oxygen carriers based on nickel [255, 256] copper oxide [224, 257, 258], iron oxide (both natural iron ore, synthetic and waste materials) [259-268], copper-iron [269, 270] and nickel-iron [271, 272]. The different forms of biomass used in those studies vary from woody biomass, pine sawdust and rice straw to biomass char and microalgae.

Experience in continuous units is limited to three installations. Table 10 provides a summary of the operating experience regarding continuous CLG installations.

The group headed by Prof. He at Guangzhou Institute of Energy Conversion (GIEC) conducted several tests in a 10 kW_{th} unit using Fe₂O₃/Al₂O₃ as the oxygen carrier and sawdust as biomass during 60 hours of operation [134, 156]. They analysed the effect of temperature and found that CO and H₂ concentrations in syngas increased with temperature and that CH₄ concentration was maintained stable at values of about 10%. Thermal cracking of biomass tar and steam reforming were found to benefit from high temperature, which caused more carbon and hydrogen to be converted into syngas. In this way, the authors obtained the highest carbon conversion (93.76%), gas yield (1.17 Nm³/kg) and cold gas efficiency (61.11 %) at a temperature of 900 °C. In addition, they analysed the effect of the lattice oxygen available for the process by varying the biomass feeding rate and maintaining a constant solid circulation rate in order to avoid fluidization problems in the system. This parameter was especially significant in this unit since more residual char was entrained into the air reactor with the increase in the biomass feeding rate. Later, they also tested an Fe₂O₃/NiO bimetallic oxygen carrier in the same unit and demonstrated its improved effect on gasification efficiency based on the synergistic effect between both metal oxides [274]. They found a maximum gasification efficiency of 70.5% with overall carbon conversion within the 71-97% range.

The group headed by Prof. Shen at Southeast University (SU) in Nanjing carried out several tests in a 25 kW_{th} unit using NiO/Al₂O₃ [135] as oxygen carriers and rice straw as biomass. They found a maximum syngas yield at 750 °C, with a NiO content of 30% in the oxygen carriers. They additionally investigated the possibility of using CaO-decorated NiO-based oxygen carriers to increase syngas yield. Later, they also tested the use of a natural haematite [275] as an oxygen carrier by analysing the effect of temperature, haematite content (diluted with silica sand) and the steam to biomass (S/B) ratio. The two first had a significant effect on the performance of the CLG process, whereas the S/B ratio had a weak effect on gas

concentrations. They demonstrated natural haematite to be an attractive oxygen carrier material for catalysing tar cracking. Optimum conditions corresponded to 860 °C, an S/B ratio of 1 and haematite content of 40%. At these conditions, a maximum syngas yield of 0.74 Nm³/kg was obtained.

The group headed by Prof. Xiao at Southeast University proposed a new technology for producing syngas or pure hydrogen based on the chemical looping pyrolysis-gasification (CLPG) process [169, 273]. The authors proposed it for the use of fuels with a high volatile content. In CLPG, the fuel reactor is divided into two zones, the pyrolysis zone and the gasification zone. The pyrolysis zone is located below the gasification zone. Steam is introduced into the middle of the fuel reactor, below the gasification zone. However, the nitrogen used for biomass pyrolysis reduced the purity of the syngas obtained. Pine sawdust was used as fuel and iron ore as the oxygen carrier. The effect of fuel reactor temperature and S/B weight ratio was analysed. At 820 °C and an S/B ratio of 1 kg/kg, they obtained a H₂/CO molar ratio of 2.45 and a cold gas efficiency of 61.87%. Increasing the S/B ratio produced an increase in the H₂/CO ratio up to values close to 3, while gas efficiency decreased.

In any CLG process, the production of other gaseous products than CO and H₂, such as CH₄ and other hydrocarbons, obviously represents a loss of efficiency. In addition, the presence of tars in the syngas stream made it necessary to use downstream cleaning processes in order to obtain a clean syngas ready for further applications. These aspects need to be addressed before further development of the technology.

5.3.3. Syngas/H₂ production by the Chemical Looping with Water Splitting process

Most of the experience regarding the CLWS process has been gained using fossil fuels, such as natural gas, coal gas and coal; however, the experience gained in the process with coal can be used for the development of this process with biofuels, such as biomass [276, 277].

Syngas, pyrolysis gases, bio-oil or bioethanol from biomass can be considered as fuels for CLWS [180, 278-282]. In this regard, a 30 kW_{th} packed bed has been constructed and operated,

demonstrating the feasibility of the concept [279]. However, major interest in the process is related to the use of biomass, namely biomass direct chemical looping (BDCL) [179, 277], which includes the circulation of solids between three reactors (fuel reactor, steam reactor and air reactor), with the fuel reactor being a moving bed with fuel feeding in the middle of the reactor [70], or a fluidized bed [283].

Few works have been found using renewable fuels in this process for hydrogen generation. Zeng et al. [284] carried out the CLWS process in a 0.6 kW_{th} unit for the production of H₂ from pine sawdust using natural haematite as the oxygen carrier. In this case, a low degree of combustion was observed in the fuel reactor. But the authors proposed mixing the gases from the fuel reactor, characterized by a high CO content, with the H₂ produced in the steam reactor, thus obtaining a syngas with a high H₂/CO ratio. In an improved configuration, Luo et al. showed that full conversion of biomass could be achieved inside a moving bed reactor, with the light tar from biomass being converted by the Fe-based oxygen carrier [138]. Further, theoretical works highlight the relevance of low moisture content, e.g. <10% [285] or even <5% [179], in order to make the process viable.

5.3.4. Opportunities of solid biofuels in chemical looping processes

The great opportunity for the thermal conversion of solid biofuels in chemical looping processes lies the way that heat can be recovered. In thermochemical processes, some heat must be recovered from the exhaust gases, with the aim of producing either heat/electricity or hydrogen/syngas,. Heat recovery will naturally be higher in combustion (iG-CLC, CLOU) than in gasification processes (CLG, CLWS), with additional heat usually being extracted from hot solids in the air reactor. In all these processes, the fuel is only used in a part of the whole process, explicitly the fuel reactor. Thus, problems related to the general use of biomass are focused only on the fuel reactor. Fouling or corrosion due to pernicious compounds in biomass such as Na-, K- and Cl-salts, or even unconverted tars, would not be expected anywhere other than in the fuel reactor. The air reactor would be then free of these compounds. As a

consequence, the heat exchangers in the air reactor and in the exhaust pipes downstream of the air reactor can be constructed of cheaper materials than those used in conventional biomass conversion processes. In addition, the temperature of the pipes, and therefore of the working fluid, can be higher, which implies an increase in thermal and energetic efficiency by using supercritical or ultra-supercritical steam cycles.

Woody biomass and agricultural residues are suitable fuels for combustion technologies, although they can be also used for H_2 /syngas production. However, the use of other solid biofuels in energy generation, such as sewage sludge or algae, can be penalized due to their high moisture content. In these cases, H_2 production via CLG may be more suitable. In this sense, algae are highly efficient at converting solar energy into chemical energy, which would boost the use of bioenergy in a decarbonized energy setting [286]. In CLG for H_2 production, a syngas is first produced, mainly consisting of H_2 and CO , and then converted into H_2+CO_2 via a water-gas shift reaction by adding steam to the gas mixture. Therefore, the fuel itself provides the required water, and a deep desiccation of the fuels would not be required, with consequent energy savings. However, a study on the optimized moisture content must be conducted in a techno-economic analysis of the CLG process.

In the chemical looping with water splitting (CLWS) process, H_2 can be generated with intrinsic CO_2 capture because H_2 , CO_2 and spent air are obtained in separated streams. In this sense, there is promising potential for negative CO_2 emissions in H_2 generation from biomass feedstock [179]. Fe-based materials have suitable characteristics for use as oxygen carriers in the CLWS process. The CLWS unit must be carefully designed in order to maximize H_2 yield by selecting fuel, steam and oxygen carrier flows, as well as to minimize the air requirements in the air reactor, which must act as a riser to allow particle circulation.

In any case, the system configuration and materials to be used with solid biofuels is highly dependent on the chemical looping process considered. The system of two interconnected fluidized beds would be preferred for CLC and CLG. In addition, the low or zero sulphur content

in most solid biofuels allows the use of oxygen carriers based on Cu, Fe, Mn, etc. or even CLOU materials, without the problems caused by material deactivation. However, consideration should be given to the interaction between oxygen carriers and alkaline compounds. In contrast, oxygen carriers based on iron are the preferred choice for the CLWS process because of their special characteristics for oxidation with H_2O to produce H_2 . In this case, the use of moving beds in the fuel and steam reactors is recommended for better exploitation of the oxygen carrier and fuel [287]. Mention should also be made of the high potential of some impregnated materials over perovskites for this CLWS process [288-290].

6. Future trends

To date, the use of biofuels in chemical looping processes has benefited from the experience gained in the use of fossil fuels, such as natural gas and coal. However, the important benefits of using biofuels to comply with the agreed goals of the Paris Agreement can boost the development of technologies with high potential for achieving negative CO_2 emissions, as is the case of chemical looping processes. Accordingly, these technologies may have a great opportunity within an appropriate and global CO_2 market, where the sale of rights for CO_2 removed from the atmosphere can make the process profitable and attractive for investors.

However, if negative CO_2 emissions are not feasible due to difficulties in the transport or storage of CO_2 , the produced bio- CO_2 can be used in the local area. In this case, the neutral property of the bio- CO_2 would facilitate the stabilization of atmospheric CO_2 concentrations. For example, the combustion of biomass in a rural area by chemical looping would produce CO_2 that can be used as a fertilizer in greenhouses or as an inert gas for pest control during the storage of agricultural products. Also, biofuels can be produced by implementing solar or wind energy for the use of bio- CO_2 .

In general, the development of chemical looping is expecting the scale-up of the process. However, some specific questions should be addressed and resolved before the use of biofuels

in chemical looping can be implemented at an industrial scale. Many of these challenges are closely linked to oxygen carrier development. Table 11 gives a summary of the most suitable oxygen carriers for each process.

Synthetic fuels are preferred for the combustion of gaseous fuels due to their higher reactivity. They might be more expensive than natural oxygen carriers, but the fact that no ashes are generated in the combustion process favours its use, as they will not be lost during ash drainage. Oxygen carriers similar to those used with gaseous fuels can be used for liquid fuel combustion, together with some Fe or Mn-based minerals. For solid fuel combustion, the right choice of oxygen carrier depends on the process considered. Minerals or residues are preferred in iG-CLC due to their low cost, taking into account the fact that some of the oxygen carrier will be lost during ash drainage. In the case of biofuels, this loss will not be as large as that occurring in coal ash drainage, as biomass ashes are expected to be separated by the cyclone. It is also possible to use Cu-based synthetic carriers as well as Fe or Mn-based minerals. Synthetic materials should be used in the CLOU process. Despite their price, they allow 100% combustion efficiency to be achieved, which is a great advantage in biomass combustion. Nevertheless, the lifetime of CLOU oxygen carriers should be augmented in order for the process to become competitive. In CLG, the preferred materials are Fe-based minerals together with some additives to avoid syngas combustion. Finally, Fe-based materials are always the choice for the CLWS process.

Chemical looping combustion of gaseous and liquid biofuels has the highest short-term expectations for the scaling-up. Several oxygen carriers previously developed for natural gas combustion are available, and no major problems have been encountered during the operation of pilot CLC units at laboratory scale.

Although the combustion of solid biofuels by chemical looping returns high CO₂ capture rate values, the further development of both iG-CLC and CLOU processes would be required before their scale-up. Should the CO₂ capture rate not be high enough, a carbon separation unit

would be required to separate unconverted char inside the fuel reactor from the oxygen carrier stream going to the air reactor. The design characteristics of the carbon separation unit when biomass is used as fuel must be evaluated in the future.

In iG-CLC, a significant fraction of volatile matter is not converted owing to poor contact with the oxygen carrier particles. It should be taken into account that the CLC units used at laboratory scale to burn biomass are not optimized for the treatment of this type of solid fuel. The fuel reactor is designed as bubbling fluidized beds, preventing high conversion of the volatile matter in biomass, which is produced in considerably larger amounts than in the case of coal. The high demand for pure oxygen to finalize the combustion of the gases from the fuel reactor may hinder the development of this technology. In order to increase the combustion efficiency of the process, the use of more reactive materials, including synthetic materials, or the implementation of technological solutions are options that can be explored in the future.

Meanwhile, the best option to avoid an oxygen polishing step is the CLOU process. In CLOU, complete CO₂ capture and fuel combustion has been demonstrated with biomass. However, the development of durable oxygen carrier materials is a key factor for the progress of the CLOU process. Consequently, the lifetime of the particles is being improved by optimizing both the composition of the oxygen carrier particles and operating conditions to in order to prolong particle durability.

The recovery of the oxygen carrier material becomes a critical issue when synthetic materials are used. It is expected that some oxygen carrier material would be lost in the ash purge stream. The recovery of the oxygen carrier particles would then be necessary in order to minimize the need for a compensatory flow of new material. In this sense, the magnetic properties of some compounds, such as Mn-Fe mixed oxides, may be useful for this purpose.

In addition, the possible negative effect of ash on oxygen carrier particles, e.g. agglomeration or deactivation, must be evaluated. In general, no critical damage to the oxygen carrier particles has been observed, but long operating periods must be achieved in the future under

similar conditions to those existing in a chemical looping unit. For this reason, the experience gained in the oxygen carrier-aided combustion (OCAC) process can be of great interest. In the OCAC process, biomass can be burned in a fluidized bed using an oxygen carrier as bed material. In this case, the combustion efficiency of the process is improved, although combustion is performed with air, and CO₂ capture is not the purpose of the process. The OCAC process is easy to scale up, and operational experience can offer information on what happens to the oxygen carrier particles during their long exposure to ash in a combustion environment.

Chemical looping gasification with biomass has great potential for producing H₂ with high CO₂ capture rates, but there are still plenty of fundamental and technical challenges to be addressed. One key aspect is the development of a cost-effective oxygen carrier suitable for CLG conditions. High resistance to carbon deposition, deactivation and agglomeration is especially important for these oxygen carrier particles. Other aspects are the evaluation of the quality of the syngas produced, the development of suitable oxygen carrier material and the optimization of the operating conditions in order to minimize the presence of hydrocarbons, e.g. CH₄ or tars. In this sense, bi-functional oxygen carrier particles, with the capability to transfer oxygen to the fuel but also with catalytic reforming activity, would be a good choice.

Some specific characteristics of biomass should be considered for the operation of a CLWS unit. A lower fraction of fixed carbon, together the high reactivity of the biochar, facilitates the complete conversion of char in the fuel reactor. However, the higher volatile matter content must be taken into account in order to fully convert volatiles to CO₂ and H₂O in the fuel reactor. What is more, carbon deposition on the oxygen carrier particles must be avoided. It should be noted that any carbon formation on the particles will be gasified in the subsequent steam reactor of the CLWS unit, which will reduce hydrogen purity because it is mixed with CO. The study of the oxygen carrier behaviour during sustained operation in CLG and CLWS processes is of great importance because a lower oxygen carrier-to-fuel ratio is adopted, at

which the risk of agglomeration significantly increases due to the reducing atmospheres present in the fuel reactor.

Overall, biomass-fuelled chemical looping processes (CLPs) are considered a very promising technology both for heat/electricity and H_2 /syngas production to achieve negative CO_2 emissions at low cost and with inherent CO_2 capture. The availability of biomass can promote the development of CLP at a lower scale than is used for fossil fuel conversion. Therefore, the development and design of bio-CLP would take place in parallel with the development of CLP for fossil fuels.

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Table 1. Operational BECCS projects (Taken from ref. [17])

Name	Operation	Capacity (Mt CO ₂ /year)	Capture	Storage
Arkalon CO ₂ Compression Facility (KS, USA)	2009	0.18-0.29	Ethanol production	Enhanced Oil Recovery
Bonanza Bioenergy (Garden City, KS, USA)	2011	0.1-0.15	Ethanol production	Enhanced Oil Recovery
Rotterdam Climate Initiative (Rotterdam, NL)	2011	0.1	Ethanol production	Greenhouses (CCU)
Husky Energy Lashburn and Tangleflags CO ₂ Injection (Lloydminster, SK, CA)	2012	0.09-0.1	Ethanol production	Enhanced Oil Recovery
Illinois Industrial CCS (Decatur, IL, USA)	2017	1.0	Ethanol production	Geological (saline formation)

Table 2. Generic advantages and disadvantages of using bioenergy.

Advantages	Disadvantages
ANY BIOFUEL	
<ul style="list-style-type: none"> • Renewable energy: reserves no limited in time • Its use virtually does not affect to the carbon balance in the atmosphere: potential for negative CO₂ emissions with CCS 	<ul style="list-style-type: none"> • Competition with food supply • Dispersed resource. Adequate for small combustion units
GASEOUS	
<ul style="list-style-type: none"> • Siloxanes removal not necessary in CLC of biogas • Possibility of dry reforming for syngas production 	<ul style="list-style-type: none"> • Lower calorific value due to the CO₂ dilution • Presence of impurities (H₂S, siloxanes, and N₂)
LIQUIDS	
<ul style="list-style-type: none"> • Suitable for use in transport (neutral CO₂ emissions in transport) • Absence of or very low sulphur contents. No deactivation catalyst in reforming processes • Bioethanol is suitable for H₂ production via CLR with CO₂ capture (negative emissions). 	<ul style="list-style-type: none"> • Not intended for heat/electricity production with CO₂ capture • Intensive purification steps needed for water removal in bioethanol used in transport
SOLIDS	
<ul style="list-style-type: none"> • Highly reactive for the conversion processes • Low ash content • Clean fuel: low sulphur and mercury content 	<ul style="list-style-type: none"> • Availability depends on natural factors: soil, climate • Energy and cost intensive for its growing, handling, transport and treatment • Low energy density, mainly due to its high moisture content and O/C ratio • Low ash melting point • Problematic fuel in a boiler: presence of alkaline metals in ash

Table 3. Typical compositions of biogas and other gaseous fossil fuels.

	Biogas	Sour gas	Natural gas. Pipeline grade
CH ₄	40-60	60-90	85-96
C ₂ -C ₅	0	0-20	≈4
CO ₂	25-50	>10	≈1
N ₂	0-15	0	≈0.8
O ₂	0-4	0	
H ₂ S	0-1	10-30	
H ₂	0-1		
NH ₃	0.01-1		
CO	0-1		
Siloxanes	traces	0	

Table 4. Main milestones in chemical looping technology.

	Year	Milestones	Authors	Institution	Initial	Ref.
Gaseous fuels						
CLC	1951	Process for carbon dioxide production	Lewis et al.		-	[96]
	1954	Production of pure carbon dioxide	Lewis & Gilliland	Standard Oil Development Company	SODC	[97]
	1983	Identification of the advantages of the process for energy production	Richer & Knoche		-	[98]
	1987	Introduction of the concept (name) of chemical looping combustion (CLC)	Ishida et al.	Tokyo Institute of Technology	TIT	[99]
	1994	Preparation and testing of first oxygen carriers	Ishida & Jin	Tokyo Institute of Technology	TIT	[100]
	1994		Ishida et al.	Tokyo Institute of Technology	TIT	[101]
	2001	First proposal of the CLC process for CO ₂ capture using fluidized bed technology	Lyngfelt et al.	Chalmers University of Technology	CUT	[102]
	2002	Proof of concept for operation in a continuous unit burning gaseous fuels	Ishida et al.	Tokyo Institute of Technology	TIT	[103]
	2004	First operation in a continuous fluidized bed unit burning gaseous fuels	Lyngfelt et al.	Chalmers University of Technology	CUT	[104]
	2005	100 h of continuous operation with a Ni-based oxygen carrier	Lyngfelt	Chalmers University of Technology	CUT	[105]
	2006	Long term operation (200 h) with Cu-based oxygen carriers	Adánez et al.	Instituto de Carboquímica (CSIC)	ICB-CSIC	[106]
	2007	Introduction of the concept of fixed bed CLC process	Noorman et al.	University of Twente	UT	[84]
	2008	Introduction of the concept of moving bed CLC process	Li & Fan	Ohio State University	OSU	[107]
	2009	1000 h of continuous operation with a Ni-based oxygen carrier in a 10 kW _{th} unit	Shulman et al.	Chalmers University of Technology	CUT	[108]
	2009	Scale-up to 120 kW _{th} CLC	Kolbitsch et al.	Technical University of Viena	TUV	[109]
	2010	First operation at pressure (10 bar)	Wang et al.	Xi'an Jiaotong University	XJU	[110]
	2010	Proof of concept for fixed bed operation	Noorman et al.	University of Twente	UT	[85]
	2013	First operation in a pressurised fixed bed	Spallina et al.	Politecnico of Milano	PM	[111]
	2014	First successful CLC operation with sour gas (H ₂ S) without deactivation of the oxygen carrier using Fe-based materials	de Diego et al.	Instituto de Carboquímica (CSIC)	ICB-CSIC	[112]
	2017	Scale-up to 1 MW _{th} CLC	Olehmueller et al.	Darmstadt University of Technology	TUD	[113]
CLR	2003	Introduction of the concept of Chemical Looping Reforming (CLR)	Zeng et al.	BOC Group	BOC	[114]
	2004	First proposal of the CLR process in fluidized beds	Ryden et al.	Chalmers University of Technology	CUT	[115]
	2006	Proof-of-concept for CLR in fluidized beds	Ryden et al.	Chalmers University of Technology	CUT	[116]

	2010	First CLR tests at pressurised conditions (10 bar)	Ortiz et al.	Instituto de Carboquímica (CSIC)	ICB-CSIC	[117]
	2010	Scale-up to 140 _{th} kW CLR	Pröll et al.	Technical University of Viena	TUV	[118]
Liquid fuels						
CLC, CLR	2009	First operation with liquid fuels in CLC	Forret et al.	IFP		[119]
	2012	First CLOU operation in a continuous unit	Moldenhauer et al.	Chalmers University of Technology	CUT	[120]
	2012	First CLR operation in a continuous unit	Moldenhauer et al.	Chalmers University of Technology	CUT	[121]
	2014	Scale-up to 10 kW _{th} CLC	Moldenhauer et al.	Chalmers University of Technology	CUT	[122]
	2015	First CLR operation with bioliquids in a continuous unit	García Labiano et al.	Instituto de Carboquímica (CSIC)	ICB-CSIC	[123]
	2016	First CLC operation with bioliquids in a continuous unit	de Diego et al.	Instituto de Carboquímica (CSIC)	ICB-CSIC	[124]
	2017	First CLC operation with heavy oil in a continuous unit 10 kW _{th} unit	Moldenhauer et al.	Chalmers University of Technology	CUT	[125]
Solid fuels						
iG-CLC, CLOU	2006	Introduction of concept of CLC for solid fuels	Cao & Pan	Western Kentucky University	WKU	[126]
	2008	First <i>in situ</i> Gasification CLC (iG-CLC) operation in continuous units	Berguerand et al.	Chalmers University of Technology	CUT	[127]
	2009	First iG-CLC operation with biomass in a continuous unit	Shen et al.	Southeast University	SU	[73]
	2009	Introduction of the concept of Chemical Looping with Oxygen Uncoupling (CLOU)	Mattisson et al.	Chalmers University of Technology	CUT	[69]
	2009	Introduction of the CaSO ₄ /CaS as redox pair for coal CLC	Andrus	ALSTOM Power	AP	[128]
	2012	Proof of concept for CLOU in fluidized beds	Abad et al.	Instituto de Carboquímica (CSIC)	ICB-CSIC	[129]
	2012	Scale-up to 1 MW _{th}	Orth	Darmstadt University of Technology	TUD	[130]
	2012	Scale-up to 3 MW _{th} for the CaSO ₄ /CaS redox system	Abdullaly et al.	ALSTOM Power	AP	[78]
	2014	First biomass-fuelled CLOU in a continuous unit	Adánez-Rubio et al.	Instituto de Carboquímica (CSIC)	ICB-CSIC	[131]
	2015	Scale-up to 1 MW _{th} using biomass as fuel	Strohle et al.	Darmstadt University of Technology	TUD	[132]
CLG	2006	First Chemical Looping Gasification (CLG) operation	Matsuoka et al.	Energy Technology Research Institute	ETRI	[133]
	2014	First CLG operation with biomass in a continuous 10 kW _{th} unit	Huseyin et al.	Chinese Academy of Sciences	CAS	[134]
	2015	Scale-up to 25 kW _{th}	Huijin et al.	Southeast University	SU	[135]
CLWS	2008	Introduction of the concept of Chemical Looping Water Splitting (CLWS)	Fan	Ohio State University	OSU	[136]
	2013	First CLWS operation with syngas in a moving bed	Tong et al.	Ohio State University	OSU	[137]
	2013	First CLWS operation with biomass in a moving bed	Luo et al. (Fan)	Ohio State University	OSU	[138]
	2015	First CLWS operation with coal in a moving bed	Fan et al.	Ohio State University	OSU	[80]

Table 5. Summary of chemical looping continuous units.

	Center/Company	Initial	Location	Configuration FR-AR	Power (kW)	Process	Biofuel	Ref.
Gaseous fuels								
1	Chalmers University of Technology	CUT	Gothenburg (Sweden)	BFB-BFB	0.3	CLC, CLR		[139, 140]
2	Instituto de Carboquímica (CSIC)	ICB-CSIC	Zaragoza (Spain)	BFB-BFB	0.5	CLC, CLR		[141, 142]
3	Chalmers University of Technology	CUT	Gothenburg (Sweden)	BFB-CFB	10	CLC		[105]
4	Instituto de Carboquímica (CSIC)	ICB-CSIC	Zaragoza (Spain)	BFB-BFB	10	CLC		[106]
5	IFPEN	IFP-TOTAL	Lyon (France)	BFB-BFB-BFB	10	CLC		[74]
6	Xi'an Jiatong University	XJU	Shaanxi (China)	BFB-CFB	10	CLC		[110]
7	ALSTOM Power Boilers	APB	France	BFB-CFB	15	CLC		[143]
8	Korean Institute of Energy Research	KIER 1	Daejeon (Korea)	BFB-CFB	50	CLC		[144]
9	Korean Institute of Energy Research	KIER 2	Daejeon (Korea)	BFB-BFB	50	CLC		[71]
10	NETL / U.S DOE	NETL	Morgantown, WV (USA)	BFB-TFB	50	CLC		[145]
11	Technical University of Viena	TUV	Vienna (Austria)	CFB-CFB	120	CLC, CLR		[109, 118]
12	SINTEF Energy Research	SINTEF	Trondheim (Norway)	CFB-CFB	150	CLC		[146]
Liquid fuels								
13	Chalmers University of Technology	CUT	Gothenburg (Sweden)	BFB-BFB	0.3	CLC, CLR		[121]
14	Instituto de Carboquímica (CSIC)	ICB-CSIC	Zaragoza (Spain)	BFB-BFB	1	CLC, CLR	YES	[123, 124]
15	Chalmers University of Technology	CUT	Gothenburg (Sweden)	BFB-CFB	10	CLC		[122]
Solid fuels								
16	Southeast University	SU	Nanjing (China)	SB-CFB	1	iG-CLC	YES	[147]
17	Instituto de Carboquímica (CSIC)	ICB-CSIC	Zaragoza (Spain)	BFB-BFB	1.5	iG-CLC, CLOU	YES	[129, 148]
18	Ohio State University	OSU	Columbus, OH (USA)	MB-EB	2.5	iG-CLC		[149]
19	Huazhong University of Science and Technology	HUST	Wuhan (China)	CFB-CFB	5	iG-CLC		[150]
20	Chalmers University of Technology	CUT	Gothenburg (Sweden)	BFB-CFB	10	iG-CLC, CLOU	YES	[127, 151]
21	Southeast University	SU	Nanjing (China)	SB-CFB	10	iG-CLC	YES	[152]
22	IFPEN	IFPEN	Lyon (France)	BFB-BFB-BFB	10	iG-CLC		[153]
23	Institute of Combustion and Power Plant Technology	IFK	Stuttgart (Germany)	CFB-CFB	10	iG-CLC		[154]

24	Western Kentucky University	WKU	Bowling Green, KY(USA)	BFB-CFB	10	iG-CLC	YES	[155]
25	Guangzhou Institute of Energy Conversion	GIEC	Guangzhou (China)	BFB-CFB	10	iG-CLC, CLG		[134, 156]
26	Hamburg University of Technology	HUT	Hamburg (Germany)	2-step BFB-CFB	25	iG-CLC	YES	[75]
27	Ohio State University	OSU	Columbus, OH (USA)	MB-EB	25	iG-CLC		[157]
28	Southeast University	SU	Nanjing (China)	CFB-CFB	50	iG-CLC		[158]
29	Instituto de Carboquímica (CSIC)	ICB-CSIC	Zaragoza (Spain)	CFB-CFB	50	iG-CLC	YES	[159]
30	VTT Research Center	VTT	Espoo (Finland)	BFB-CFB	50	iG-CLC	YES	[160]
31	Huazhong University of Science and Technology	HUST	Wuhan (China)	CFB-CFB	50	iG-CLC		[161]
32	Chalmers University of Technology	CUT	Gothenburg (Sweden)	CFB-CFB	100	iG-CLC	YES	[162]
33	Japan Coal Energy Center	JCOAL	Tokyo (Japan)	CFB-CFB	100	iG-CLC		[163]
34	SINTEF Energy Research	SINTEF	Trondheim (Norway)	CFB-CFB	150	iG-CLC	YES	[164]
35	University of Utah	UU	Salt Lake City, UT (USA)	CFB-CFB	225	iG-CLC		[165]
36	Babcock & Wilcox	B&W	-	MB-EB	250	iG-CLC		[166]
37	Darmstadt University of Technology	TUD	Darmstadt (Germany)	CFB-CFB	1000	iG-CLC	YES	[167]
37	ALSTOM Power	AP	Bloomfield, CT (USA)	CFB-CFB	3000	iG-CLC		[78]
39	Chalmers University of Technology	CUT	Gothenburg (Sweden)	BFB-CFB	4000	iG-CLC	YES	[168]
40	Southeast University	SU	Nanjing (China)	BFB-CFB	0.6	CLG	YES	[169]
41	Southeast University	SU	Nanjing (China)	BFB-CFB	25	CLG	YES	[135]

Table 6. Summary of the processes involving biofuels and chemical looping technology.

Fuel	Process	Main features
Combustion		
Gaseous	Biogas-CLC	<ul style="list-style-type: none"> - Oxygen carriers available for scale-up - No expected problems with sulphur or siloxanes in biogas
Gaseous	Syngas-CLC	<ul style="list-style-type: none"> - Prior gasification of solid fuel - Oxygen requirement for gasification - The solid fuel is not mixed with oxygen carrier particles - Ash-oxygen carrier interaction is prevented
Gaseous	Pyrolysis gas-CLC	<ul style="list-style-type: none"> - Previous pyrolysis of solid fuel - N₂ in pyrolysis gases negatively affects CO₂ capture - Biochar can be deposited in soil as carbon storage - Careful design due to high-volume gas expansion during fuel conversion
Liquid	CLC	
Solid	iG-CLC	<ul style="list-style-type: none"> - Gasification of the solid fuel inside the fuel reactor - Low cost oxygen carriers are desirable - A final oxygen polishing step is necessary
Solid	CLOU	<ul style="list-style-type: none"> - Use of oxygen carriers with gaseous O₂ release properties - Rapid and efficient conversion of the solid fuel - Possible interaction between ash and oxygen carrier - An oxygen carrier recovery step is preferred
Syngas / H₂ production		
Gaseous	Biogas-CLR	<ul style="list-style-type: none"> - Oxygen carriers with catalytic activity are desirable - Gas cleaning required (H₂S) to avoid catalytic deactivation
Gaseous	tar-CLR	<ul style="list-style-type: none"> - Prior gasification/pyrolysis of solid fuel - Reforming of tar and volatile organic compounds - Oxygen carriers with catalytic activity are desirable
Liquid	CLR	<ul style="list-style-type: none"> - Oxygen carriers with catalytic activity are desirable - High H₂ yield - Tunable H₂/CO composition - Can be coupled to a sorption-enhanced process - Pyrolysis oils or bio-oils can be used to obtain valuable products - Pure N₂ can be obtained in the air reactor
Solid	CLG	<ul style="list-style-type: none"> - Partial oxidation of solid fuel with oxygen carriers - Process can be adapted to produce a pure N₂ stream and the desired CO/H₂ ratio
Solid	CLWS	<ul style="list-style-type: none"> - Separated streams of H₂, CO₂ and N₂ can be obtained - Highly pure H₂ can be achieved - Specific Fe-based oxygen carriers are used

Table 7. Summary of biofuels used in chemical looping processes and status of development. (LS=Laboratory scale, CU= tests in continuous units).

		Combustion			Syngas production			
		CLC	iG-CLC	CLOU	CLR	CLR+SE	CLG	CLWS
Gaseous	- biogas	LS			LS			
	- biomass-derived syngas	LS			CU			CU
	- biomass volatiles from torrefaction	LS						
Liquids	- ethanol	CU			CU			
	- waste cooking oil				LS	LS		
	- glycerol				LS	LS		
	- bio-oil from pyrolysis				LS			CU
Solids	- pine sawdust /wood chips		CU	CU			CU	CU
	- olive stones		CU	CU				
	- almond shells		CU	CU				
	- biochar / wood char		CU	CU			LS	
	- sewage sludge		CU					
	- co-combustion (solid biofuel+ coal)		CU					
	- rice husks, rice straw						CU	
	- algae, microalgae						LS	

Table 8. Experimental conditions for CO₂ capture efficiency and oxygen demand from different iG-CLC and CLOU continuous units.

Name	Nominal power (kW)	Oxygen carrier	Fuel	FR design	Fuel reactor Temperature (°C)	Carbon capture (%)	Oxygen demand (%)	Operation (h)	Ref.
IG-CLC									
ICB-CSIC	0.5	Iron ore	pine sawdust	Bubbling	880-980	90-100	7-34.6	37 + 14	[231, 232]
ICB-CSIC	0.5	Iron ore	olive stones	Bubbling	905-980	90-100	20-30	13.4	[232]
ICB-CSIC	0.5	Iron ore	almond shell	Bubbling	905-985	90-100	18-28	10.8	[232]
SU	1	Iron ore	Shenhua bituminous coal/ Sawdust	Spouted	720-930	95.5-98.5	<i>n.a.</i>	-	[233]
SU	1	Haematite	Sewage sludge	Spouted	800-900	~ 100	8.5-23.5	10	[234]
SU	1	Haematite	sewage sludge (SS) and Zhundong (ZD) coal	Spouted	800-930	94-96	13.5-35	5	[235]
SU	10	Iron oxide	Pine sawdust	Spouted	740-920	<i>n.a.</i>	<i>n.a.</i>	30	[73]
CUT	10	Manganese ores	Wood char	Bubbling	887-1000	76.0-96.4	5.8-11.4	32	[236]
VTT	50	ilmenite	White&black pellets	Bubbling	~850	83-96	29-41	16	[160]
CUT	100	Ilmenite	Wood char	High vel.	929-973	91-97	4.7-15.5	31	[237]
CUT	100	Iron ore (Tierga)	Wood char	High vel.	880-960	>96	7.4-8.5	26	[238]
TUD	1000	Iron ore (Tierga)	Hard coal&torrefied biomass	High. Vel.	900-950	Up to 66	38-45	37	[239]
CUT	4000*	Ilmenite/manganese ores	wood pellets	CFB	~830	<i>n.a.</i>	Combustion eff.~60% Charconv.~40%	>1000	[168]
CLOU									
ICB-CSIC	1.5	CuO/MgAl ₂ O ₄	Pine sawdust	Bubbling	900-935	98-100	0	10	[131]
ICB-CSIC	1.5	Cu-Mn	Pine sawdust	Bubbling	775-850	86-100	0	20	[240]
ICB-CSIC	1.5	Cu-Mn	olive stone	Bubbling	775-850	78-91	0	10	[240]
ICB-CSIC	1.5	Cu-Mn	almond shell	Bubbling	775-850	73-93	0	10	[240]
CUT	10	CaMn _{0.9} Mg _{0.1} O ₃₋₆	Biochar	Bubbling	917-970	82-95.2	2.1-4.9	-	[151]

* Corresponds to the gasifier acting as fuel reactor in the Chalmers boiler/gasifier loop (with inputs of 12 MW_{th} and 2–4 MW_{th}, respectively)

Table 9. Summary of the CLOU oxygen carriers tested with solid biofuels at laboratory scale

Metal oxide	Oxygen carrier	Fuel	Reactor	Ref.
CuO	CuO/MgAl ₂ O ₄ (40/60 wt%)	devolatilized wood char	Batch FB	[222]
	CuO	biomass (rice hull, candlenut wood)	TGA	[223]
	Cu /MgAlO ₂ O ₄	walnut shell	TGA, fixed bed	[224]
Cu-Mn mixed oxides	5, 10, 20, 31, and 61 wt % CuO	devolatilized wood char	Batch FB	[230]
Perovskite	Manganese ores + Ca(OH) ₂	wood char	Batch FB	[227]
Mn-Fe mixed oxides	(Mn _{0.8} Fe _{0.2}) ₂ O ₃	devolatilized wood char	Batch FB	[228]
Mn-Si-Ti mixed oxides	(75% Mn ₃ O ₄ 25% SiO ₂)	wood char	Batch FB	[229]
	(66.7% Mn ₃ O ₄ , 22.2% SiO ₂ , 11.1% TiO ₂)			

Table 10. Summary of chemical looping gasification continuous units.

Name	Nominal power (kW)	Oxygen Carrier	Fuel	Configuration	Operating conditions		Ref.
					FR temperature (°C)	Steam/Biomass ratio (%)	
SU	0.6*	Iron ore	Pine sawdust	Dual FB gasifier	700-880	0.5-3	[169]
SU	0.6*	Iron ore	Pine sawdust	Dual FB gasifier	700-880		[273]
GIEC	10	Fe ₂ O ₃ /Al ₂ O ₃	Pine sawdust	Interconnected FB	670-900	n.a.	[134]
GIEC	10	Fe ₂ O ₃ /NiO	Pine sawdust	Interconnected FB	760-910		[156]
SU	25	Ni-based, CaO-decorated NiO/Al ₂ O ₃	Rice straw	Interconnected FB	650-850	0.4-2.0	[274]
SU	25	natural haematite	Biomass (rice husk)	Interconnected FB	800-900	0.6-1.4	[135]
							[275]

Table 11. Summary of the most suitable oxygen carriers for each process using biofuels. (S= synthetic, M= mineral, ad= additives).

	Gaseous		Liquids		Solids			
	CLC	CLR	CLC	CLR	iG-CLC	CLOU	CLG	CLWS
Ni		S		S				
Cu	S		S		S	S		
Fe	S		S,M		M		S+ad,M+ ad	S,M
Mn					M			
Mn-Fe	S		S		S	S		
Cu-Mn						S		
Ca-Mn						S		