

From post-combustion carbon capture to sorption-enhanced hydrogen production: A state-of-the-art review of carbonate looping process feasibility

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ABSTRACT

Carbon capture and storage is expected to play a pivotal role in achieving the emission reduction targets established by the Paris Agreement. However, the most mature technologies have been shown to reduce the net efficiency of fossil fuel-fired power plants by at least 7% points, increasing the electricity cost. Carbonate looping is a technology that may reduce these efficiency and economic penalties. Its maturity has increased significantly over the past twenty years, mostly due to development of novel process configurations and sorbents for improved process performance. This review provides a comprehensive overview of the calcium looping concepts and statistically evaluates their techno-economic feasibility. It has been shown that the most commonly reported figures for the efficiency penalty associated with calcium looping retrofits were between 6 and 8% points. Furthermore, the calcium-looping-based coal-fired power plants and sorption-enhanced hydrogen production systems integrated with combined cycles and/or fuel cells have been shown to achieve net efficiencies as high as 40% and 50–60%, respectively. Importantly, the performance of both retrofit and greenfield scenarios can be further improved by increasing the degree of heat integration, as well as using advanced power cycles and enhanced sorbents. The assessment of the economic feasibility of calcium looping concepts has indicated that the cost of carbon dioxide avoided will be between 10 and 30 € per tonne of carbon dioxide and 10–50 € per tonne of carbon dioxide in the retrofit and greenfield scenarios, respectively. However, limited economic data have been presented in the current literature for the thermodynamic performance of calcium looping concepts.

1. Introduction

Decarbonisation of the power sector, which is responsible for a third of the anthropogenic greenhouse gas (GHG) emissions [1], is critical to meeting the targets established by the Paris Agreement that recommended keeping the global mean temperature increase below 2 °C and undertaking efforts to limit it to 1.5 °C above pre-industrial levels to significantly reduce the risks and impacts of climate change [2]. Transformation of this sector is essential to meet both environmental and energy demand targets, while ensuring sustainable utilisation of natural resources and keeping the cost of electricity at an affordable level. Despite the potential improvements in their efficiency, unabated conventional fossil fuel-fired power generation systems are not able to meet these environmental targets. As there are no other technologies

that could significantly reduce emissions from fossil fuel-fired power generation systems, which are expected to remain in the electricity mix for the foreseeable future, carbon capture and storage (CCS) is seen as crucial to decarbonising the power sector [3]. Importantly, the 2DS scenario assumes that CCS will contribute to nearly 14% reduction in global carbon dioxide (CO₂) emissions by 2050 [4]. It has also been estimated that the exclusion of CCS may increase the cost of achieving emission reduction targets by up to 70% [5].

Although considerable progress has been made in reducing the energy intensity of mature CO₂ capture and separation technologies, these are still expected to reduce the net efficiency of the reference power generation system by at least 7% points [6,7]. This corresponds to at least 60% increase in the electricity cost [8], hindering the deployment of CCS in the power sector. It also needs to be highlighted that such a

Abbreviations: 2DS, 2°C scenario; AC, cost of CO₂ avoided; ASU, air separation unit; CaL, carbonate looping; CaLC, carbonate looping combustion; CCS, carbon capture and storage; CCU, CO₂ compression unit; CFPP, coal-fired power plant; CPU, CO₂ purification and compression unit; GHG, greenhouse gas; HEN, heat exchanger networks; IGCC, integrated-gasification combined cycle power plant; IGFC, integrated-gasification fuel cell; NGCC, natural gas combined cycle power plant; LCOE, levelised cost of electricity; SESR, sorption-enhanced steam reforming process; SEWGS, sorption-enhanced water-gas shift; SOFC, solid-oxide fuel cell; ZECOMAG, zero-emissions coal mixed technology with air gas turbine; ZECOMIX, zero-emissions coal mixed technology

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Nomenclature

Subscripts

el	electrical energy
th	thermal energy
gross	value based on gross power output
vol	value on volumetric basis

reduction in the net efficiency was found to impose the largest impact on the environmental performance of mature CO₂ capture and separation technologies, as it will result in increased fuel consumption to achieve the same net power output. In turn, it will affect the upstream processes associated with extraction, preparation and transportation of fuels [9]. As a result, CCS is predicted to result in 64% [10] to 80% [11] reduction of GHG emissions over the entire system lifetime even though it is commonly designed to remove 90% of CO₂ from combustion of fossil fuels [10]. Therefore, less energy-intensive technologies, such as high-temperature solid looping cycles, are currently being developed [12]. Carbonate looping (CaL), which is based on the reversible carbonation reaction of CO₂ with a metal oxide, such as calcium oxide (CaO) or magnesium oxide (MgO), is regarded as an emerging technology for decarbonisation of fossil fuel power generation systems [6]. This is because it has been shown not only to reduce the efficiency penalties, but also to increase the net power output of the retrofitted system [7]. The main reason behind such improvement, when compared to the mature CO₂ capture and separation technologies, is the high-temperature operation of CaL, enabling high-grade heat to be recovered, as well as clean and efficient syngas generation.

Application of CaL for decarbonisation of fossil fuel-fired power generation systems was first proposed two decades ago by Hirama et al. [13] and Shimizu et al. [14]. Since then, this concept has been

developed via both experimental testing and thermodynamic modelling [7]. It needs to be highlighted that significant developments have been achieved after 2009 that led to demonstration of CaL at the megawatt scale: the 1 MW_{th} unit in Darmstadt [15], the 1.7 MW_{th} unit in Oviedo (La Pereda) [16], and the 1.9 MW_{th} unit at the Industrial Technology Research Institute (ITRI), Taiwan [17]. The development of CaL has been regularly reviewed with respect to a range of progress activities as summarised in Table 1. These focused on the experimental and pilot plant testing activities [7,18,19], sorbent performance and development [6,18–27], process modelling [7,25,28,29], and CaL configurations for fossil fuel-fired power plants [7,20,28] and hydrogen production [19]. As can be seen in Table 1, the recent studies focused mostly on developments in CaL retrofits to existing fossil fuel-fired power generation systems, rather than on novel greenfield power plants utilising CaL-based combustion and sorption-enhanced hydrogen (H₂) production processes. Moreover, emphasis was put on improvements from the process thermodynamics and sorbent development standpoints. It is crucial, however, to understand whether such performance improvements are substantiated by the improvements in the economic performance that will support commercial deployment of CaL. Therefore, to build on the previous reviews in this field, this work aims to guide further development of the high-efficiency low-emission fossil fuel-fired power generation and hydrogen production systems based on CaL by:

- comprehensively reviewing progress in the development of CaL concepts for retrofitting conventional fossil fuel-fired power generation systems;
- providing a comprehensive overview of greenfield power generation concepts based on CaL combustion and sorption-enhanced hydrogen production processes; and
- conducting a statistical evaluation of the techno-economic feasibility of CaL concepts using data available in the current literature.

Table 1
Summary of review studies related to the carbonate looping process.

Source	Publication date	Review scope
Stanmore and Gilot [27]	2005	<ul style="list-style-type: none"> • Summary of the sintering, sulphation, particle fragmentation and attrition effect on sorbent activity • Detailed information on the correlations for mathematical modelling of carbonation, calcination, sulphation and sintering • A brief overview of the models for prediction of the aerodynamics and trajectories of particles, as well as reaction rates in the circulating fluidised bed
Harrison [21]	2008	<ul style="list-style-type: none"> • Comparison of the standard steam-methane reforming process and the CaL process for hydrogen production • Review of the thermodynamic analyses, sorbent durability and process configurations • Review of the experimental studies on hydrogen production
Florin and Harris [19]	2008	<ul style="list-style-type: none"> • Review of process configurations for enhanced hydrogen production from biomass gasification • Summary of sorbent regeneration measures • A brief reference to sorbent activity decay
Blamey et al. [25]	2010	<ul style="list-style-type: none"> • Review of experimental trials on hydrogen production from carbonaceous fuels using carbonate looping • Detailed description of the carbonation, calcination, sintering and sorbent performance under repeated cycle operation • Summary of sorbent deactivation and reactivation measures • Review of the carbonate looping process applications
Dean et al. [18]	2011	<ul style="list-style-type: none"> • A brief summary of semi-empirical correlations allowing estimation of the sorbent conversion • Summary of carbonate looping cycle fundamentals, sorbent deactivation and sorbent performance • Review of the carbonate looping thermodynamic and economic performance, as well as its applicability in the cement industry and to hydrogen production • A brief reference to sorbent activity decay
Anthony [26]	2011	<ul style="list-style-type: none"> • Review of the pilot plant trials for CaL • Review of sorbent performance improvements and reactivation strategies for natural and synthetic sorbents
Liu et al. [24]	2012	<ul style="list-style-type: none"> • Brief outline of carbonate looping process applicability and experimental facilities • Review of sorbent performance enhancements • Review of synthesis methods for sintering-resistant sorbents
Kierzkowska et al. [23]	2013	<ul style="list-style-type: none"> • Summary of the carbonation reaction fundamentals • Review of recent developments in synthesis of CaO-based sorbents
Romano et al. [28]	2013	<ul style="list-style-type: none"> • Review of CaL process simulations and notes on further modelling activities
Boot-Handford et al. [6]	2014	<ul style="list-style-type: none"> • Summary of process performance, sorbent deactivation and regeneration • An update on CaL pilot-plant trials
Hanak et al. [7]	2015	<ul style="list-style-type: none"> • Review of test facilities worldwide and testing activities • Review of the modelling approaches • Review of CaL process configurations for improved process integration

(continued on next page)

Table 1 (continued)

Source	Publication date	Review scope
Martinez et al. [29]	2016	<ul style="list-style-type: none"> ● Review of the modelling activities worldwide ● Indication of research needs for further development of CaL
Perejon et al. [20]	2016	<ul style="list-style-type: none"> ● Review of multicyclic sorbent behaviour ● Role of energy integration and sorbent behaviour on process efficiency
Erans et al. [22]	2016	<ul style="list-style-type: none"> ● Review of techniques to enhance natural sorbent performance and to synthesise new sorbents ● Review of measures to reactivate and reuse deactivated sorbent

2. Carbonate looping process

Since being patented in 1933, development of CaL has mainly focused on sorption-enhanced hydrogen production [21] and CO₂ capture from fossil fuel-fired power generation systems [14]. In both applications, the most commonly considered process configuration comprises two interconnected circulating fluidised beds (Fig. 1) that, when linked with a heat exchanger network, is characterised with thermal efficiency similar to that of current combustion systems [30]. Therefore, as opposed to other CCS technologies, high-temperature operation of CaL allows high-grade heat to be utilised in the secondary power cycle for additional power generation. If CaL was retrofitted to an existing fossil fuel-fired power generation system, the net power output of the entire process was shown to increase by more than 50% [31].

In the first reactor, the so-called carbonator, CO₂ is removed from flue gas or syngas on contact with metal oxide (Me_xO), which has been previously calcined in the calciner, via an exothermic solid-gas reaction. The carbonation process takes place at an elevated temperature, which varies between 450 °C (magnesium-based sorbents [32]) and 700 °C (calcium-based sorbents [33]), depending on the sorbent used in CaL and the partial pressure of CO₂ entering the carbonator. Under such conditions, CO₂ is removed from syngas or flue gas as metal carbonate (Me_xCO₃) at a reasonably high rate. Importantly, the carbonation process will only take place below the temperature corresponding to the equilibrium partial pressure of CO₂ in the syngas or flue gas [34]. The metal carbonate is then regenerated in another reactor, the so-called calciner, and CO₂ is reclaimed [35]. Again, the temperature at which the calcination takes place depends on the CO₂ partial pressure and type of sorbent fed to the calciner. In pure CO₂ at atmospheric pressure, this varies between 550 °C for magnesite and dolomite (partial calcination) [32], to 900 °C for dolomite (complete calcination) and limestone [33]. Under such operating conditions, a pure CO₂ stream can be theoretically achieved. Although higher operating temperatures would favour reaction kinetics, these would lead to enhanced sorbent sintering and, thus, deterioration of its CO₂ capture capacity. Importantly, the calciner can be operated at lower temperatures if steam, which can be easily separated by condensation from the CO₂ steam, is injected as a diluent. A reduction in the sorbent CO₂ carrying capacity on cycling operation as a result of sintering, attrition and sulphation is regarded as the major challenge of CaL. To maintain acceptable sorbent conversion in the carbonator, the spent sorbent needs to be partially replaced by fresh sorbent [18].

In the conventional configuration of CaL (Fig. 1), an additional amount of fuel is combusted in an oxygen/carbon dioxide (O₂/CO₂) environment to maintain the desired operating temperature in the calciner and produce a high-purity CO₂ stream. Therefore, the power required to drive the air separation unit (ASU), in addition to the CO₂ compression unit (CCU), is the main source of the parasitic load in CaL. Further reduction in the efficiency penalty associated with this technology can be achieved by reducing, or even avoiding, the need for oxygen production in the energy-intensive ASU [36]. Alternative options to provide heat for sorbent regeneration include chemical looping [37–40], which uses oxygen carriers to transfer oxygen from an air reactor to the calciner, and indirect heat transfer from a combustor via

solid heat carriers [41,42], heat transfer wall [42,43] or heat pipes [44,45].

3. Retrofits to conventional power generation systems

The existing fossil fuel-fired power generation capacity is highly dependent upon coal. However, this trend has begun to change recently and natural gas combined cycle (NGCC) power plants are expected to play an essential role in the future energy portfolio. This is mostly because of their capability for rapid changes in the operating load that will be essential to balance the energy supply and demand in the energy market with a large share of intermittent renewable energy sources [46]. Although NGCCs are characterised by lower specific CO₂ emissions compared to coal-fired power plants (CFPPs), they still need to be decarbonised for the emission reduction targets to be met by 2050. Having been considered for sorption-enhanced hydrogen production since 1933 [21], application of CaL for CO₂ capture from fossil fuel power plants was proposed for the first time by Shimizu et al. [14] in 1999. Since then, a number of CaL concepts have been proposed for decarbonisation of both CFPPs (Section 3.1) and NGCCs (Section 3.2).

3.1. Coal-fired power plants

Shimizu et al. [14] were the first to evaluate the feasibility of a CaL retrofit to a supercritical CFPP. The high-grade heat available in CaL was used to produce superheated and reheated steam at subcritical conditions. Overall, the net efficiency of the retrofitted system was estimated to be 33.4%. This was 1.4% points higher than for an oxy-fired combustor with a primary steam cycle of the same gross power output

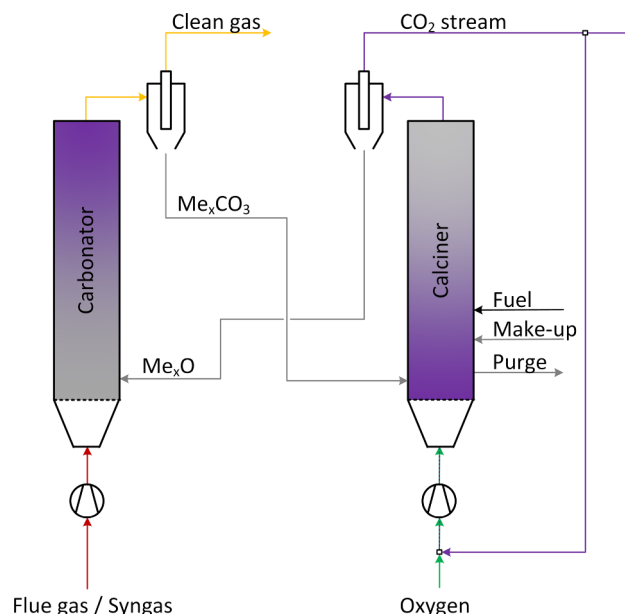


Fig. 1. Operating principle of carbonate looping for carbon capture.

and, thus, indicated the feasibility of the CaL process for reducing CO₂ emissions from CFPPs. Although this study did not provide a direct benchmark of the CaL retrofit to the reference CFPP, it stimulated other researchers to further evaluate the feasibility of such systems.

Romeo et al. [47] have investigated the retrofit of CaL to a 450 MW_{el} supercritical CFPP. Importantly, this study assumed that, in contrast to oxy-fuel combustion systems, no CO₂ recirculation was needed to control the temperature in the calciner because of the large solid inflow at 650 °C and the endothermic character of the calcination reaction. A detailed evaluation of the process configuration revealed that there were five heat integration zones that could utilise the high-grade heat from the carbonator and process streams to generate high-pressure steam and preheat the feedwater in the secondary steam cycle. Although this increased the net power output of the integrated system by 45.3%, the net efficiency dropped by 7.9% points, from 44.9% for the reference CFPP. The feasibility of the concept of CaL with no CO₂ recirculation has been confirmed by Hanak et al. [48]. The thermodynamic assessment of CaL retrofitted to the 580 MW_{el} supercritical CFPP revealed that the efficiency penalty was not affected by the level of CO₂ recirculation and was estimated to be 7.5% points. This is because, on reduction of the CO₂ recirculation from 52.8%, which corresponded to the oxygen concentration in the gas stream entering the calciner of 30%_{vol}, to zero, the net power output of the entire system and the total coal consumption were found to be reduced at the same level. Furthermore, the feasibility of the CaL retrofit to CFPPs was confirmed by Hawthorne et al. [49], Strohle et al. [50,51] and Lasheras et al. [52] who evaluated the CaL retrofits to an 1100 MW_{el} supercritical CFPP. Upon the CaL retrofit the net efficiency of the entire system was reduced by 6.3% points, from 45.6% for the reference CFPP, while the net power output increased by 45.7% [49]. Importantly, the studies by Strohle et al. [50,51] and Lasheras et al. [52] revealed that the efficiency penalty associated with CaL without CCU amounted to 2.7–3.2% points that mainly stem from the requirement for oxygen separation in the cryogenic ASU. It needs to be noted that the lower efficiency penalties reported in these studies resulted from the secondary steam cycle being operated under supercritical conditions, as opposed to the sub-critical conditions considered by Romeo et al. [47]. In this vein, Martinez et al. [53], who evaluated the CaL retrofit to both sub-critical and supercritical CFPPs, indicated that the efficiency penalties would be smaller for CaL retrofitted to supercritical CFPPs.

The studies reviewed previously assumed that the calciner is fuelled with the same fuel as the reference CFPP. A study by Hanak et al. [31]

evaluated the effect of fuel used in the calciner on the efficiency penalty of the CaL retrofit to a 580 MW_{el} supercritical CFPP. This study revealed that partial (20%) and complete substitution of coal with biomass in the calciner can lead to reduction in the efficiency penalty from 7.9% points to 7.7% and 7.4% points, respectively. This is primarily a result of lower CO₂ capture level in the calciner, as biomass can be considered as a CO₂-neutral fuel, and less ash being circulated in the system; hence less heat required for solids preheating in the calciner. A large reduction in the efficiency penalty to 6.7% points was also observed for the case of a natural gas-fired calciner, which was primarily due to no ash accumulation in the system. It must be stressed that the reviewed studies indicated that the CaL retrofits would result in lower efficiency penalty compared to chemical solvent scrubbing, which was shown to result in efficiency penalty of 9% points (chilled ammonia scrubbing) [54] and 9.5% points (monoethanolamine scrubbing) [31] when retrofitted to the same CFPP. Nevertheless, all of the reviewed studies assessing the CaL retrofitted to the CFPP concluded that the main sources of the parasitic load result from the power requirement of the ASU and the CCU. For this reason, the main reduction in the efficiency penalty associated with CaL can be primarily achieved via reduction of the heat requirement in the calciner, utilising alternative options to provide heat for sorbent regeneration and thus avoiding the need for oxygen production in the energy-intensive ASU.

A wide range of measures for reduction of the efficiency penalty associated with CaL retrofits to CFPPs has been reported in the literature. These measures focus primarily on improving the heat integration within both the CaL process itself, and between CaL and CFPP. This aims at reducing the heat requirement in the calciner and increasing the degree of heat utilisation in the entire system. Such an improvement can be realised via application of a systematic heat exchanger network (HEN) analysis, which is regarded as an industrial standard to maximise the heat utilisation within the system. Lara et al. [55,56] have employed such an approach to maximise the techno-economic performance of the CaL retrofit to a 500 MW_{el} supercritical CFPP, which was characterised with the net efficiency of 38.2%. Their studies have shown that the efficiency penalty can be reduced from 6.4% points to between 5.2% points [55] and 6.2% points [56] on an improvement in the heat integration of the entire system. Moreover, a study by Vorrias et al. [57], which evaluated the retrofit of CaL to a 330 MW_{el} supercritical CFPP using lignite as a fuel, has indicated that heat integration has the potential to significantly reduce the efficiency penalty. Primarily, deployment of a solid-solid heat exchanger (Fig. 2a), which

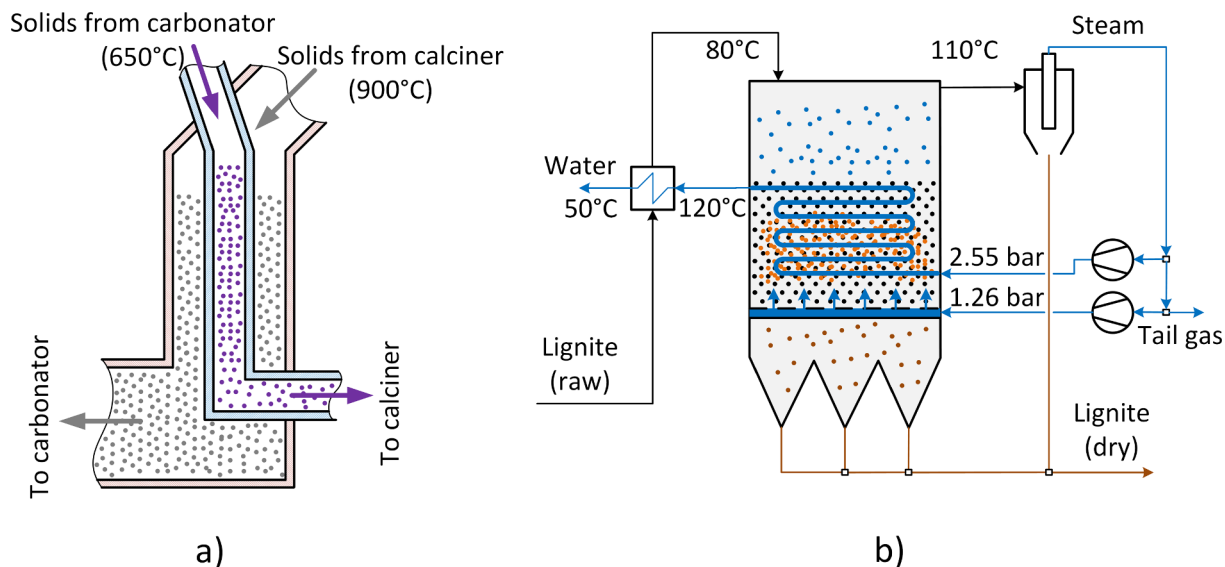


Fig. 2. Representation of (a) solid-solid heat exchanger and (b) lignite bubbling fluidised bed dryer (Adapted with permission from Vorrias et al. [57]. Copyright 2013 Elsevier.).

allows preheating the solids entering the calciner against the solids leaving the calciner, was shown to reduce the heat requirement from fuel oxy-combustion in the calciner. As a result, the efficiency penalty associated with such a system was found to be 5.1% points. Further improvement of 0.1% point was achieved via implementation of a lignite dryer (Fig. 2b) that utilised recompressed steam as a fluidising medium and was designed to reduce the moisture content in lignite to a level comparable to that of hard coal [58]. Again, the efficiency penalty estimated for the CaL retrofit was shown to be 2.9% points lower compared to that of a corresponding CO₂ capture plant using chemical solvents (monoethanolamine) and 0.9% points lower than that of an oxy-fuel CFPP using lignite as a fuel. This has further proved the thermodynamic benefits of CaL retrofits to CFPPs compared to other CO₂ capture technologies. In this vein, a study by Ortiz et al. [59] has shown that the efficiency penalty associated with the retrofit of CaL to a 561 MW_e subcritical CFPP, which is characterised with a net efficiency of 33.5%, can be improved by 0.2% points on implementation of a solid-solid heat exchanger. Such an improvement arose primarily from both a reduction in the fuel and oxygen requirements in the calciner, which can be lower by up to 16.5%, and a 2% point increase in the thermal efficiency of CaL according to a study by Martínez et al. [60]. However, technically and economically feasible devices for heat transfer between two solid phases must first be developed.

Alternative concepts that utilise existing and industrially proven equipment were proposed by Martínez et al. [60,61]. The first concept included a single mixing seal valve for both the carbonator and the calciner that allows direct heat transfer between the solids leaving these reactors [60]. This configuration was deemed as bringing no thermodynamic improvement over the conventional CaL process, primarily due to reduced fraction of active CaO entering the carbonator. The second concept included an additional heat recovery fluidised bed, in which the sensible heat of the CO₂ stream leaving the calciner is recovered to preheat the solid particles from the carbonator [60]. Although the concentrated CO₂ stream mixed with the partially carbonated solid particles from the carbonator, no carbonation reaction could occur. This is because the fast carbonation reaction cannot proceed, as

the active CaO is trapped in the core of each solid particle, the surface of which has been covered with the calcium carbonate (CaCO₃) layer formed in the carbonator [62]. Despite the fact that the heat requirement in the calciner was still satisfied via direct oxy-fuel combustion, the fuel and oxygen requirements would be reduced by up to 9.7%, and the thermal efficiency of CaL can be improved by 1.4% points. The third concept utilised cyclonic preheaters, which are used in the cement industry, in place of the heat recovery fluidised bed (Fig. 3) [61]. In this additional piece of equipment, heat available in the CO₂ stream leaving the calciner was utilised to preheat solids leaving the carbonator to around 725 °C prior to entering the calciner. Although implementation of the cyclonic preheater has not changed the net efficiency of the retrofitted system, it reduced the energy requirement of the calciner. This was shown in reduction of the coal and oxygen requirements by up to 13.3%, with respect to the conventional CaL process.

Regardless of the potential for a significant reduction in the heat requirement, and thus fuel and oxygen requirements in the calciner, the concepts reviewed above still require the energy-intensive and expensive cryogenic ASU for direct oxy-fuel combustion in the calciner. Interestingly, this requirement can be completely alleviated by indirect heat transfer from another heat source. Abanades et al. [42] proposed an alternative design of the calciner in which the heat for sorbent regeneration is supplied through the metallic walls from a fluidised bed combustor fueled with an air and fuel mixture that operates at 1050 °C. In such a design, the calciner can be operated at 850 °C, which is lower than the temperature of 875–950 °C considered in the previous studies, as steam was used as the fluidising medium. Yet, although this configuration would be characterised by higher thermal efficiency and no requirement for oxygen production, it would require materials that have not yet been tested in practice. Also, close integration of the combustor and the calciner is required, as a considerable heat transfer area of 800 m² is required. Despite the engineering challenges, this configuration was reported to impose an efficiency penalty of 6.6% points, which is 1.6% points less than for the conventional CaL configuration. More recently, the use of heat pipes as a mean for indirect heat transfer between the calciner and the combustor, which operated

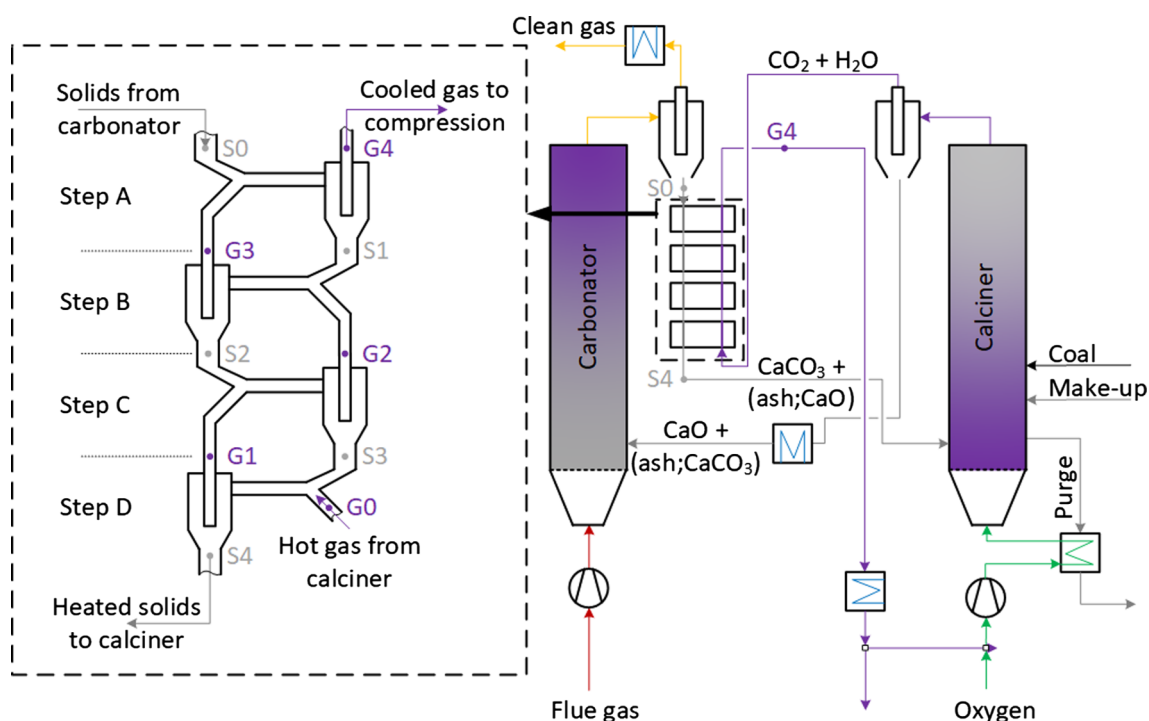


Fig. 3. Improvement of carbonate looping process performance through implementation of the cyclonic preheater (Adapted with permission from Martínez et al. [61]. Copyright 2013 American Chemical Society.).

at 1100 °C, have been experimentally proven [44]. The retrofit of such an indirectly-heated CaL to the 1100 MW_{el} supercritical CFPP was shown to result in an efficiency penalty of 1.8–2.3% points (without compression), depending on the sorbent conversion in the carbonator. This was found to be 1% point lower than the corresponding retrofit of the conventional CaL process to the same reference CFPP [45]. To avoid using untested materials, an alternative to reduce the heat requirement in the calciner is the concept of calcination driven by heat carriers that was first proposed by Abanades et al. [42]. Similarly to the concept of the indirectly-heated calciner, this process includes an additional circulating fluidised bed combustor in which fuel is burned in an excess amount of air. The bed material, which is a dense solid material such as aluminium oxide (Al₂O₃) or deteriorated sorbent, is heated up directly in the combustor, separated from the flue gas stream, and then fed to the calciner to provide heat for sorbent regeneration. However, it is still not clear whether continuous separation of the sorbent and the heat carrier based on the difference in their densities would be possible at the required scale. Nevertheless, the net efficiency of the retrofit scenario based on such a system is claimed to be 2.2% points higher than that of the conventional CaL retrofit [42]. Finally, the heat for sorbent regeneration in the calciner can be driven by the heat from a chemical looping system [40], which uses oxygen carriers to transfer oxygen from air to the fuel. The combined calcium and chemical looping system includes an additional reactor – air reactor – in which the oxygen carrier reacts with oxygen in air. The oxidised oxygen carrier is then reduced by the gaseous fuel in a fuel reactor, providing heat for calcination (Fig. 4). This system was considered to operate as either a single- or dual-loop process [38], depending on whether the oxygen carrier is mixed with the sorbent and reduced directly in the calciner, or is handled separately in another loop. In the latter case, the heat is transferred to the calciner indirectly. The efficiency penalty associated with the combined calcium and chemical looping process was estimated to be between 3.6 and 6.9% points [39] and 5.2–6.3% points [38] for the single- and dual-loop process, respectively. Although the efficiency penalty of such a process was found to be 2.5–3% points lower than that of CaL retrofitted to the same reference CFPP, the required solids looping rate to achieve the same CO₂ capture level was at least one order of magnitude higher than that in CaL [38]. This imposes an additional efficiency penalty associated with the requirement for handling more solids. Yet, such a high circulation rate was required due to the low oxygen carrier-to-sorbent ratio in the considered system. Therefore, the concept needs to be further explored considering higher content of oxygen carrier in the solid material required to meet the heat requirement for sorbent regeneration.

It must be stressed that all reviewed studies considering CaL retrofitted to CFPPs assumed that the high-grade heat is utilised to raise high-pressure steam for the secondary steam cycle. Yet, the study by Hanak et al. [63] has highlighted that CaL operates within a similar temperature range to the bottoming cycle of NGCC (600 °C), nuclear reactors (500–1000 °C), and concentrating solar power plants (500–1000 °C). Therefore, it proposed to use advanced power cycles, such as a supercritical CO₂ cycle, for utilisation of the high-grade heat from CaL. The analysis of CaL retrofitted to a 580 MW_{el} supercritical CFPP indicated that by using the supercritical CO₂ cycle in place of the supercritical steam cycle, the efficiency penalty can be reduced by 1% point, if the turbine inlet conditions are the same. On increase of the turbine inlet pressure from 242 bar to 300 bar and temperature from 593 °C to 620 °C, the efficiency penalty was further reduced by 0.6% point, to 6.3% points. Further improvement in the thermodynamic performance can be obtained via implementing an additional inter-cooling stage and replacing the first main compressor with a pump that can bring the efficiency penalty down to 5.8% points. This was shown to be 2.1% points improvement over the conventional CaL process. Therefore, consideration of advanced power cycles, such as the supercritical Brayton cycle, for utilisation of high-grade heat from CaL, has the potential for considerable reduction in the efficiency penalty

associated with this technology, especially when linked with the alternative concepts reviewed above.

The main engineering challenge of CaL, which needs to be addressed prior to commercial deployment of this technology, is degradation of the sorbent performance after a number of calcination and carbonation cycles. This can be associated primarily to sintering, attrition and sulphation of the sorbent, leading to the requirement for sorbent make-up [18]. Conversion of the sorbent can be improved via doping, thermal pre-treatment, chemical treatment, and reactivation [22].

Hydration has been proven via thermogravimetric analysis [64] and pilot-scale tests [65] as one of the most viable options to improve sorbent performance. Its benefits on the thermodynamics of the CaL retrofit to CFPPs was investigated by Wang et al. [34,35] and Hanak et al. [66]. In such a process, the sorbent is reactivated on contact with steam in the hydrator (Fig. 5). Wang et al. [34] have analysed integration of this concept into a 561 MW_{el} subcritical CFPP and high-grade heat from the CaL process was used to generate high-quality steam that is sent to the primary cycle, replacing part of the steam generated in the power boiler. This means that the existing boiler would need to operate in the part-load mode. The thermodynamic performance assessment indicated that a maximum net efficiency of 26.9% could be reached if the calciner was indirectly heated using the flue gas from the combustion process. On the other hand, when the calciner was directly heated through oxy-fuel combustion of coal or natural gas, the net efficiency decreased to 26.5% and 26.1%, respectively. Such values for net efficiency are considerably lower than those reported previously. The main reason behind this is the low net efficiency of the reference CFPP. Nevertheless, the maximum efficiency penalty was estimated to be 7.4% points, which is in line with the figures reported in other studies. Furthermore, Wang et al. [35] have shown that the efficiency penalty for the CaL process with sorbent reactivation via hydration is 22.2% lower than that for the conventional CaL process. Conversely, Hanak et al. [66] have shown that implementing the hydration concept to reactivate the sorbent would only reduce the efficiency penalty by 0.3% points, from 8.7% points to 8.4% points. As the latter process operates on higher average conversions, this reduction can be associated with reduction of the solid looping rates between the reactors, which leads to a decrease in the heat requirement in the calciner. Nevertheless, a lower improvement in the net efficiency on implementing hydration in the study by Hanak et al. [66] could be

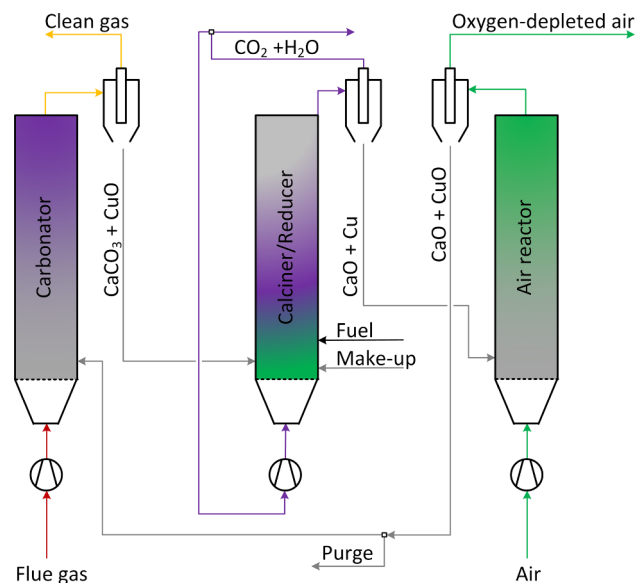


Fig. 4. Combined calcium and chemical looping single-loop process (Adapted with permission from Duhoux et al. [38]. Copyright 2016 Wiley.).

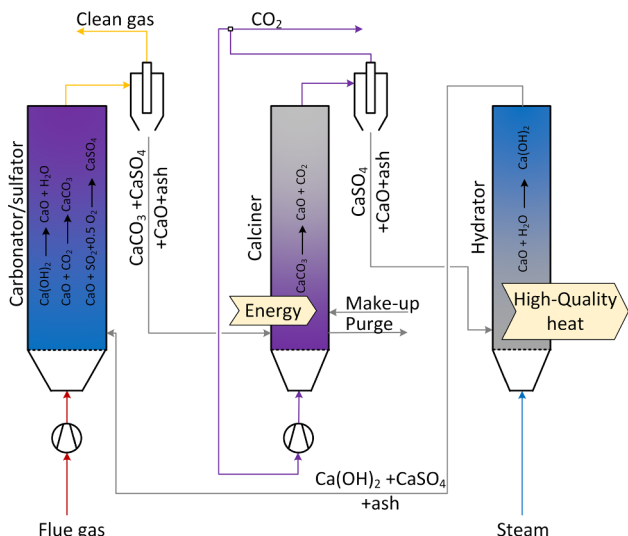


Fig. 5. Conceptual design of hydrated carbonate looping process (Adapted with permission from Wang et al. [34]. Copyright 2012 Elsevier.).

explained by the fact that the steam for hydration was taken directly from the steam cycle, rather than generated in a separate steam boiler, as was the case in the work by Wang et al. [34,35]. Overall, these studies proved that the implementation of hydration as a mean for sorbent reactivation could reduce the efficiency penalty.

In this vein, the use of alternative sorbents was also recognised as a means to improve sorbent reactivity. Ortiz et al. [67] compared the effect of using limestone, dolomite, and steel slag as a sorbent on the thermodynamic performance of the CaL retrofit to a 505 MW_{el} subcritical CFPP. Their study indicated that the heat required for the calcination is lower for dolomite and steel slag, mainly because these can

be calcined at lower temperatures (900 °C) than limestone (950 °C). However, such a reduction in the operating temperature, along with the higher inert material content in the dolomite and steel slag, resulted in the efficiency penalty being 0.3% and 0.2% point higher, respectively, than that reported for limestone (5.6% points). This is in line with the results presented by Lisbona et al. [68], who evaluated the retrofit of CaL to a 500 MW_{el} supercritical CFPP. Namely, the efficiency penalty associated with using dolomite was estimated to vary between 5.7 and 14.2% points, as opposed to 5.8% points for limestone. Again, this was associated with the inert material content in dolomite. Therefore, using alternative sorbents may not necessarily improve the thermodynamic performance of the CaL retrofit, regardless of potential improvements in the reactivity of the sorbent.

A recent study by Hanak et al. [69] adapted a stochastic approach to assess the economic feasibility of CaL retrofitted to a 580 MW_{el} supercritical CFPP. This study indicated that the most probable values for the levelised cost of electricity (LCOE) and the specific capital cost associated with the CaL retrofit were between 75 and 115 €/MW_{el}h, and 2100 and 2300 €/kW_{el, gross}, respectively. This allowed classifying the LCOE estimated in the previous economic assessments that used the deterministic approach as the best- (25.8–54.3 €/MW_{el}h) [47,70], probable- (68.4–82.5 €/MW_{el}h) [66,70–73] and worst-case scenarios (116.7 €/MW_{el}h) [74]. The specific capital cost was also categorised as the best- (1305–1738.4 €/kW_{el, gross}) [47,70,72], probable- (1812.5–2097.3 €/kW_{el, gross}) [66,70], and the worst-case scenario (3723.9 €/kW_{el, gross}) [74] estimates. Moreover, a recent study by Hanak et al. [48] has shown that the specific capital cost associated with the CaL retrofit can be reduced by up to 21.7% if no CO₂ recirculation is considered to moderate the temperature in the calciner. This corresponded to 14.3% and 27.4% reduction in the LCOE, from 74.8 €/MW_{el}h to 64.1 €/MW_{el}h, and the cost of CO₂ avoided, from 57.3 €/tCO₂ to 41.6 €/tCO₂, respectively.

Although a study by Lisbona et al. [68] indicated that using alternative sorbents may not improve the thermodynamic performance of

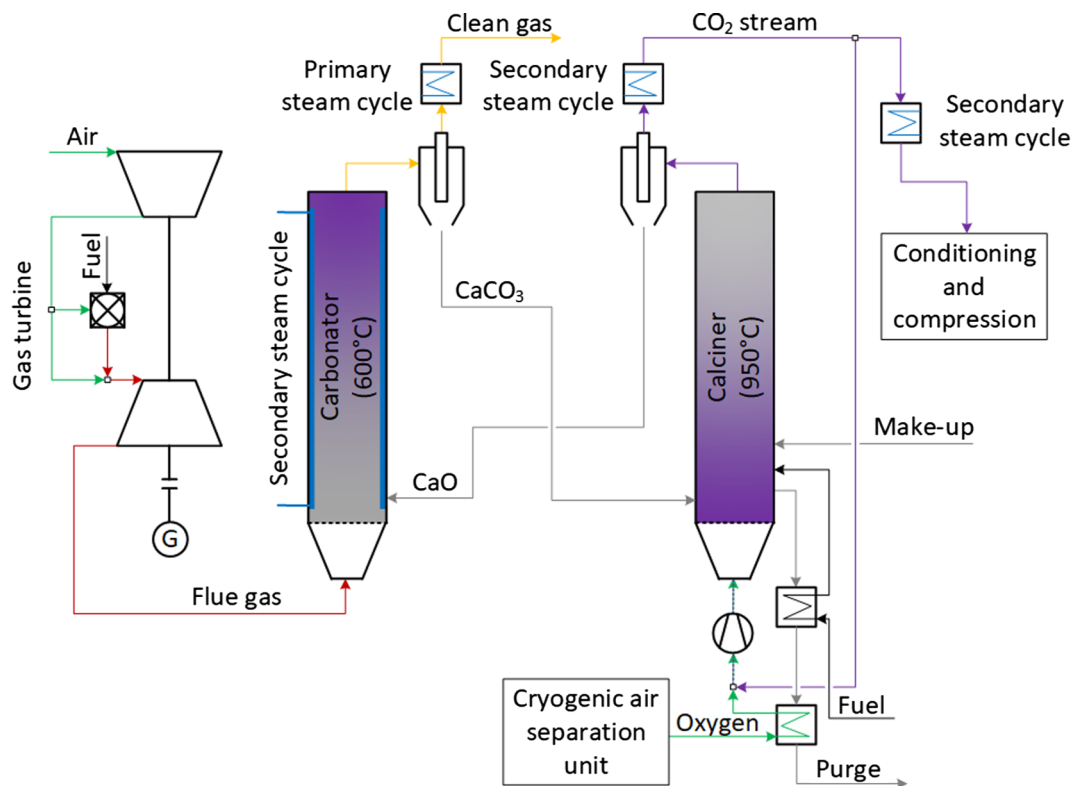


Fig. 6. Conceptual design of integration of carbonate looping to natural gas combined cycle power plant (Adapted with permission from Berstad et al. [79]. Copyright 2012 Elsevier.).

the CaL retrofit, an increase in the sorbent reactivity would reduce the amount of the sorbent required to achieve the same CO₂ capture level, and thus could result in an improvement of the economic performance. As a result, the cost of CO₂ avoided can be lower for dolomite (18.6 €/tCO₂) compared to limestone (15.8–19 €/tCO₂), under particular operating conditions. This was mostly because of the comparable prices of limestone and dolomite of 6–10 €/t. Importantly, although alumina-doped limestone and lithium orthosilicate (Li₄SiO₄) were shown to experience considerably lower degradation than natural sorbents, their high price of 240–310 €/t and 27,000 €/t, respectively, resulted in the cost of CO₂ avoided to be higher (22–300 €/tCO₂) than that of limestone and dolomite. Therefore, a substantial drop in the material cost is required for these sorbents to be used at commercial scale to ensure that the CaL retrofit is feasible from both technical and economic standpoints. Furthermore, Hanak et al. [66] showed that the techno-economic feasibility of the CaL retrofit to a CFPP would be improved upon implementation of the sorbent reactivation via hydration. This study not only indicated that such solution would result in a reduced efficiency penalty, but also in an 18% reduction in the cost of CO₂ capture and a 6% reduction in the specific capital cost. In addition, studies by Abanades et al. [70], Cormos [72], and Cormos and Cormos [73] proved that the LCOE can be reduced by increasing the steam conditions in the conventional steam cycles, hence their net thermal efficiency. Interestingly, in the latter studies [72,73], the cost of CO₂ avoided was found to increase with the steam conditions in the conventional steam cycle. This, however, can be associated to the capture rate (higher by 3.3%) in the case when CaL is retrofitted to a supercritical CFPP. Finally, the deterministic studies reviewed indicated that the cost of CO₂ avoided has the potential to be lower (7–87.5 €/tCO₂) [47,66,70–74] compared to that of mature chemical solvent scrubbing (35–75 €/tCO₂) [73,75–78], proving the potential for economic feasibility of CaL retrofits to CFPPs.

3.2. Natural gas combined cycle power plants

Berstad et al. [46,79] were the first to analyse the feasibility of retrofitting CaL downstream of the gas turbine in a 416.4 MW_{el} NGCC (Fig. 6), that was characterised with a net efficiency of 58.4%, under a range of operating conditions for the secondary steam cycle, heat integration configurations, and sorbents. The benchmark configuration that assumed the recovery of high-grade heat from CaL in the sub-critical secondary steam cycle, was shown to result in an efficiency penalty of 12.0% points. Such performance was considerably worse compared to the same NGCC retrofitted with chemical solvent scrubbing using monoethanolamine, which resulted in an efficiency penalty of 8.6% points, and indicated that a CaL plant may not be a preferable option for NGCCs. This can be attributed primarily to the low CO₂ concentration in the flue gas. The net efficiency of the CaL retrofit was found to improve by 1.7% points upon changing the operating conditions of the secondary steam cycle from sub- to super-critical, which was a result of the higher efficiency of the high-grade heat utilisation. This implies that there is the potential for further reduction in the efficiency penalty by implementing more efficient power cycles, such as the supercritical CO₂ cycle [63]. Further improvement in the net efficiency of 0.8% points was obtained on implementing the solid-solid heat recuperator, reducing the efficiency penalty to 10.0% points [79]. This was a result of reducing the temperature difference between the reactors, and thus reducing the fuel and oxygen requirements to sustain the desired calciner temperature. Importantly, oxy-combustion of natural gas in the calciner will result in a significant fraction of moisture in the gas phase inside this reactor (30–40%_{vol}). Therefore, the calciner can be efficiently operated at lower temperature [46], leading to further reduction in the temperature difference between the reactors. This modification, along with implementing hot CO₂ recycle and optimising the fresh sorbent make-up ratio, resulted in 2.9% points improvement in the net thermal efficiency, reducing the efficiency penalty to 7.1% points [46].

Such improvement in the thermodynamic performance of the CaL retrofit makes it clear that this technology can compete with more mature chemical solvent scrubbing systems.

Similarly to the study by Berstad et al. [79], Hu and Ahn [80] indicated that the retrofit of CaL to NGCC, which comprised an F-class gas turbine and sub-critical primary steam cycle, was less favourable compared to chemical solvent scrubbing using monoethanolamine. However, they proposed implementing exhaust gas recirculation to increase the CO₂ concentration in the flue gas entering the carbonator from ~4%_{vol} to ~7%_{vol}. Such configuration was found to reduce the efficiency penalty associated with the CaL retrofit from 10% points to 8.6% points. Regardless of such an improvement, the net efficiency of the CaL retrofit was still 0.9% point lower than the corresponding chemical solvent scrubbing retrofit with exhaust gas recirculation. However, if the improvement measures proposed by Berstad et al. [46,79] were implemented, a substantial reduction in the efficiency penalty below 7% points could be achieved. Yet, application of these configurations must be economically substantiated. This is because implementation of exhaust gas recirculation and supplementary firing in a chemical solvent scrubbing retrofit to a NGCC was shown to increase the capital cost by 20%, while reducing the LCOE by only 6% [81].

As indicated above, the main challenge of CaL using natural sorbents, such as limestone (calcite), is rapid degradation of sorbent performance over a number of cycles. Importantly, an increase in the average carbonation conversion from 18.6% (calcite) to 24.8% (dolomite) and 34.2% (synthetic CaO), resulted in an efficiency penalty reduction of 0.2% and 0.8% points, respectively [46]. Yet, such increase in the thermodynamic performance should be substantiated by benefits in the economic performance. This is particularly important in the case of the synthetic sorbents that are characterised by much higher specific costs [68].

Unfortunately, information on the economic feasibility of CaL retrofits to NGCCs in the current literature is limited to a few studies by Cormos and Cormos [82,83], and Erans et al. [84]. The former studies assessed the techno-economic performance of CaL retrofitted to a 498 MW_{el} NGCC comprised of an M701G2 (Mitsubishi Hitachi Power Systems) gas turbine and a subcritical primary steam cycle, with a net efficiency of 58.6%. The thermodynamic performance of the system reduced by 9.4% points on the CaL retrofit, higher than the efficiency penalty of 5.9% points reported for chemical solvent scrubbing using methyl diethanolamine. Although this is in line with the estimations made by Berstad et al. [79] and Hu and Ahn [80], Cormos and Cormos [82,83] reported that the LCOE of 56.9 €/MWh for the CaL retrofit was 16.2% lower compared to the chemical solvent scrubbing retrofit. Moreover, the cost of CO₂ avoided for the CaL retrofit (33.8 €/tCO₂) was estimated to be nearly half that for the chemical solvent scrubbing retrofit (67.1 €/tCO₂), and the specific capital cost was 30.2% lower. Similar results were presented by Erans et al. [84], who evaluated the techno-economic performance of CaL retrofitted to an 820 MW_{el} NGCC that was characterised with the net efficiency of 57.7%. This study also compared the effect of the location of CaL with respect to the primary steam cycle on the net efficiency of the system. Importantly, retrofitting the CaL downstream of the primary steam cycle resulted in a much higher efficiency penalty (12.0% points) compared to the upstream location (8.6% points). This resulted from the high volume of flue gas that needed to be preheated prior to entering the carbonator to maintain the desired operating temperature. Hence, the amount of high-grade heat available for recovery in the secondary steam cycle was lower, reducing the net efficiency of the entire system. Nevertheless, the retrofit of CaL upstream of the primary steam cycle was shown to result in a cost of CO₂ avoided of 29.3 €/tCO₂, which is comparable to the figure reported by Cormos and Cormos [82,83]. Importantly, in these studies [82–84], the LCOE increased by 25.6–33.2% with respect to that estimated for the reference NGCC without CO₂ capture.

4. Greenfield power generation systems

As has been shown above, CaL can be seen as the technically and economically feasible option to decarbonise the existing fleet of fossil fuel-fired power generation systems, especially when novel process configurations, improved sorbent performance via hydration, high degree of heat integration, and utilisation of advanced power cycles for high-grade heat recovery are considered. The main feature of CaL, however, is its high-temperature operation that creates an opportunity for this technology to act as a power boiler in novel power generation systems. This enables further reductions in the economic and efficiency penalties, as well as supports wide deployment of low-carbon power generation technologies. Therefore, similarly to the measures aimed to reduce the efficiency penalty associated with CaL retrofits to fossil fuel-fired power generation systems, a number of alternative process configurations for novel CFPPs were developed that were characterised with much lower CO₂ emissions compared to those of conventional systems (Section 4.1). Moreover, the need for high-efficiency and low-emission fossil-fuel power generation systems has led to the development of novel integrated gasification combined cycle (IGCC) power plants that have the potential to improve both thermodynamic and economic performance compared to the conventional CFPPs (Section 4.2).

Substitution of fossil fuels with biomass [4] or cost-effective production of clean fuels, such as hydrogen, is predicted to contribute towards decarbonisation of the power sector. A combination of CCS with hydrogen production is considered to be the least cost-intensive option among other hydrogen production technologies [85]. A number of sorption-enhanced steam reforming (SESR) concepts based on CaL, especially using Ca-based sorbent, have been recently developed (Section 4.3). These have been shown to significantly enhance the quality and economics of hydrogen production from reforming of liquid and gaseous fuels with simultaneous CO₂ capture [86–91]. Importantly, with NGCC being a well-established commercial technology with high efficiency and reliability, and low capital costs [90], the novel low-carbon concepts based on that technology can be expected to be characterised by more favourable techno-economic performance compared to novel CFPPs [92,93] and could become commercially available in a relatively short timeline. Yet, for such concepts to use hydrogen-rich fuel instead of natural gas, conventional gas turbines need to be adapted, mainly by reducing the operating temperatures and partially closing the compressor variable guide vanes, to consider changes in the volumetric flow rate and the thermophysical properties of hydrogen-rich fuels [94].

4.1. Combustion-based coal-fired power plants

Building on the concept proposed by Abanades et al. [42] in which the calcination process was driven by heat carriers, Martínez et al. [41] proposed a novel CFPP using a three-fluidised-bed combustion system based on CaL (Fig. 7). In this process, the heat required to calcine the sorbent was provided by heating both a part of the calcined sorbent from the calciner and fuel ash up to 1030 °C. These solids were heated in the air-fired circulating fluidised bed combustor, indicating that there was no need for energy-intensive ASU. Importantly, flue gas from the combustor was directly fed to the carbonator and, thus, the proposed process can be seen as a standalone CFPP with two heat sources (combustor and carbonator) and a single heat sink (calciner). Having integrated these heat sources, along with several hot solid and gas streams, with the supercritical steam cycle, Martínez et al. [41] have shown that the net efficiency of such a process can reach 37.8%, considering the power requirement of the CCU. This was shown to be 4.3% points higher than a comparable oxy-fired CFPP, proving the thermodynamic feasibility of this novel concept. However, it needs to be pointed out that the calcined sorbent would be exposed to temperatures higher than 1000 °C upon heating in the combustor, which may cause

enhanced sintering and deactivation [95]. Therefore, evaluation of the effect of increased sorbent deactivation on the techno-economic performance of the three-fluidised-bed combustion system based on CaL should be conducted to prove its feasibility under such operating conditions.

Strelow et al. [96] proposed integrating a pressurised calciner, which is an entrained flow reactor, inside a coal-fired combustor (Fig. 8). To enable efficient operation of the calciner under higher pressure (2–3 bar) and 900 °C, superheated steam was injected into that reactor. Importantly, in addition to utilising the high-grade heat to raise steam for the supercritical steam cycle, which is a generally used practice in the state-of-the-art CaL concepts [7], the CO₂-H₂O stream leaving the calciner at a higher pressure was used in the steam turbine to generate an additional amount of power. The assessment of the thermodynamic performance of this concept was shown to impose an efficiency penalty 4.4% points, considering the power requirement for the CCU. This further proves that indirect heat transfer can not only substantially reduce the energy intensity of the ASU, but also lead to development of novel CFPPs. Therefore, development of the indirectly-heated calciner technology has the potential to provide a substantial reduction in the energy intensity of CaL, and bring this technology closer to commercialisation [42].

In this vein, Hanak and Manovic [36] have recently proposed a calcium looping combustion (CaLC) process for high-efficiency, low-emission power generation (Fig. 9). In this process, the heat for sorbent calcination is provided indirectly from an external coal-fired combustor and the resulting flue gas is directed to the carbonator for CO₂ capture. Considering the CaLC as a power boiler, similarly to the approach applied by Martínez et al. [41], to raise high-pressure steam for the supercritical steam cycle, the net efficiency of the entire system was estimated to be between 33.7% and 35.6, which was 2.4–4.3% points lower than the reference CFPP operating under the same steam conditions. This was mainly associated with the power requirement of the CCU and the amount of high-grade heat available for power generation in the supercritical steam cycle under different operating conditions. Importantly, a reduction in the efficiency penalty in this concept compared to the concepts proposed by Martínez et al. [41] and Strelow et al. [96] can be attributed to a higher degree of heat integration in CaLC, as in this concept the heat integration between solid and gas streams, and optimisation of the fresh limestone make-up stream were considered. Such improvements are consistent with the results presented by Lara et al. [55,97] who utilised a systematic heat exchanger

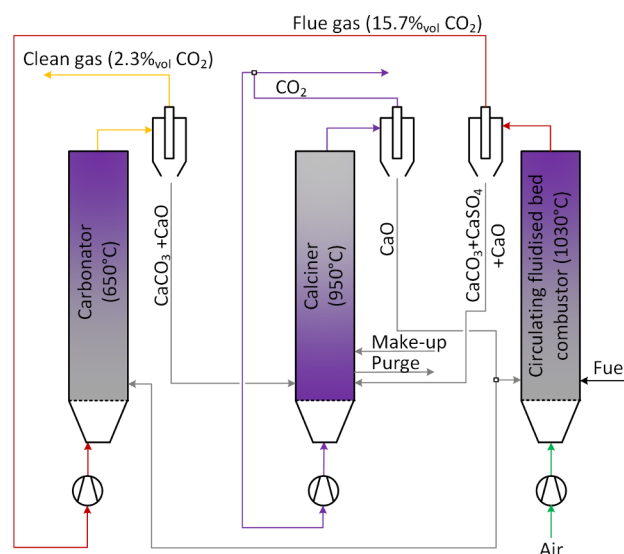


Fig. 7. Concept of the three-fluidised-bed combustion system based on carbonate looping (Adapted with permission from Martínez et al. [41]. Copyright 2011 Elsevier.).

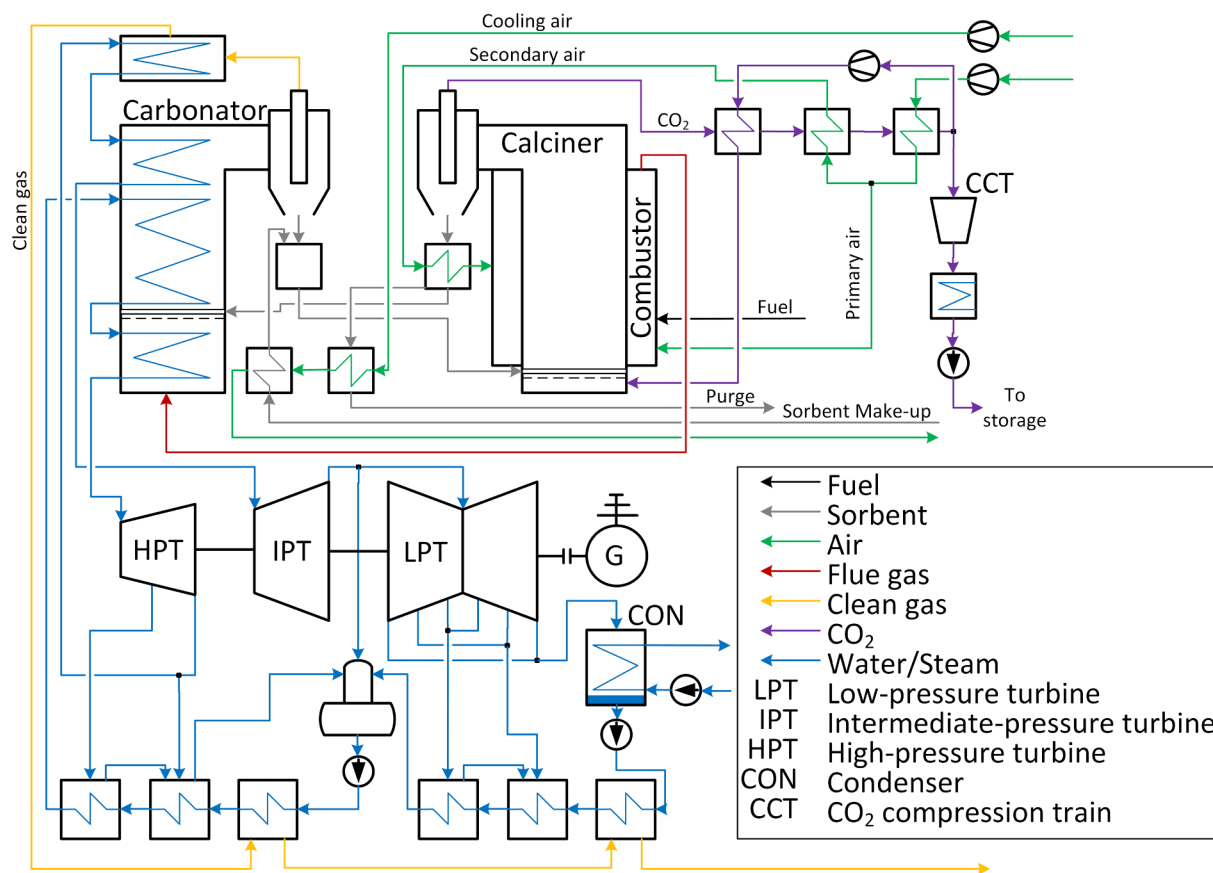
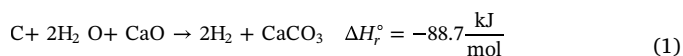


Fig. 9. Calcium looping combustion for high-efficiency low-emission power generation (Adapted with permission from Hanak and Manovic [36]. Copyright 2017 Elsevier.).

and depending on the amount of sulphur in the char, such a process can achieve a net efficiency of 41.0–41.7%. Importantly, if Ca-based sorbent modified with acetic acid was utilised, the net efficiency can reach 42.4–43.1%, while removing 90% of CO₂. Such a figure is higher compared to the range of 28.6–40.2% reported for novel combustion-based CFPPs (Section 4.1). Yet, the feasibility of using such modified sorbent needs to be substantiated from both technical and economic standpoints.

The concept evaluated by Li et al. [101] followed the state-of-the-art concepts for decarbonisation of the conventional CFPPs that were retrofitted with CaL as the post-combustion system. However, in IGCC power plants, CO₂ capture can be implemented as either a post-combustion system for CO₂ capture from flue gas, or a pre-combustion system for CO₂ capture from syngas. Therefore, it can be expected that using CaL as the pre-combustion CO₂ capture plant in an IGCC would reduce the energy requirement for sorbent regeneration due to a higher partial pressure of CO₂ in syngas compared to flue gas. Moreover, CaL has been shown to enhance the water-gas shift reaction, yielding a high-purity hydrogen stream, and thus increasing the quality of syngas [102]. This is because, in the sorption-enhanced gasification process, the net reaction of which is shown in Eq. (1), CaO will remove CO₂ produced in the water-gas shift reaction, shifting the equilibrium to the right and promoting high-purity hydrogen production [103].



The techno-economic feasibility of these concepts were compared by Cormos and Cormos [102,104], who used a 561 MW_{el} IGCC power plant characterised with a net efficiency of 44.4% as a reference. The thermodynamic assessment indicated that the net efficiency of the entire system reduced by 10.1% points and 7.3% points for the post-

combustion and pre-combustion configuration, respectively. This implied that the performance of the IGCC with CaL for the post-combustion CO₂ capture was comparable with that associated with conventional post-combustion scrubbing technologies. Hence, similarly to retrofits of conventional CaL to NGCC evaluated by Berstad et al. [46,79] and Erans et al. [84], such application of this technology will not bring any benefits in terms of process thermodynamic performance. Conversely, the pre-combustion configuration was found to result in an efficiency penalty 1–2% points lower than conventional pre-combustion solvent scrubbing technologies. Furthermore, the economic assessment has confirmed the superiority of the pre-combustion configuration, as the associated LCOE and cost of CO₂ avoided for this configuration were 76.1 €/MW_{el,h} and 26.3 €/tCO₂, compared to 78.1 €/MW_{el,h} and 29.2 €/tCO₂ for the post-combustion configuration, respectively [84]. It needs to be pointed out that the economic performance, including the specific capital cost, is comparable to that of the CaLC concept proposed by Hanak and Manovic [36]. Therefore, the pre-combustion configuration has been deemed as a more suitable for IGCC power plants and has been further evaluated.

A study by Wang et al. [105] analysed an IGCC power plant fueled with high-purity hydrogen produced via sorption-enhanced gasification of coal in a dual-fluidised-bed system (Fig. 12). In such a system, the gasifier reactor was divided in two sections, a gasification section, in which allothermal steam gasification of coal took place, and a carbonation section, where carbon monoxide (CO) was shifted to CO₂ that was then removed on contact with CaO. It has been assumed that only part of the coal was converted in the gasifier reactor (45–60%) and the unreacted char was fed to the calciner. Oxy-combustion of that amount of fuel was shown to be sufficient for sorbent regeneration in the calciner. The high-purity hydrogen stream was then utilised in an F-class gas turbine and the high-grade heat was converted into electricity in a

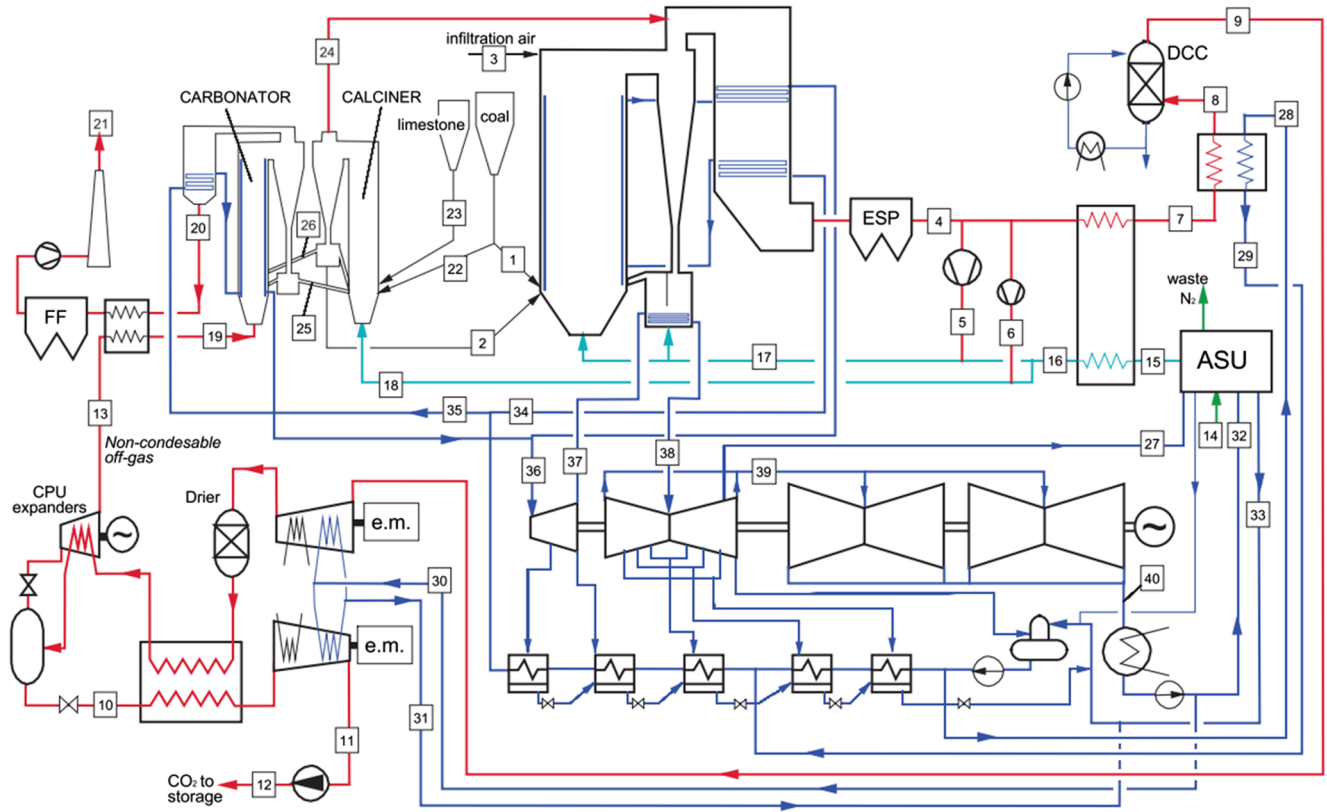


Fig. 10. Conceptual design of circulating fluidised bed oxy-fuel ultra-supercritical power plant with carbonate looping (Reprinted with permission from Romano [99]. Copyright 2013 Elsevier.)

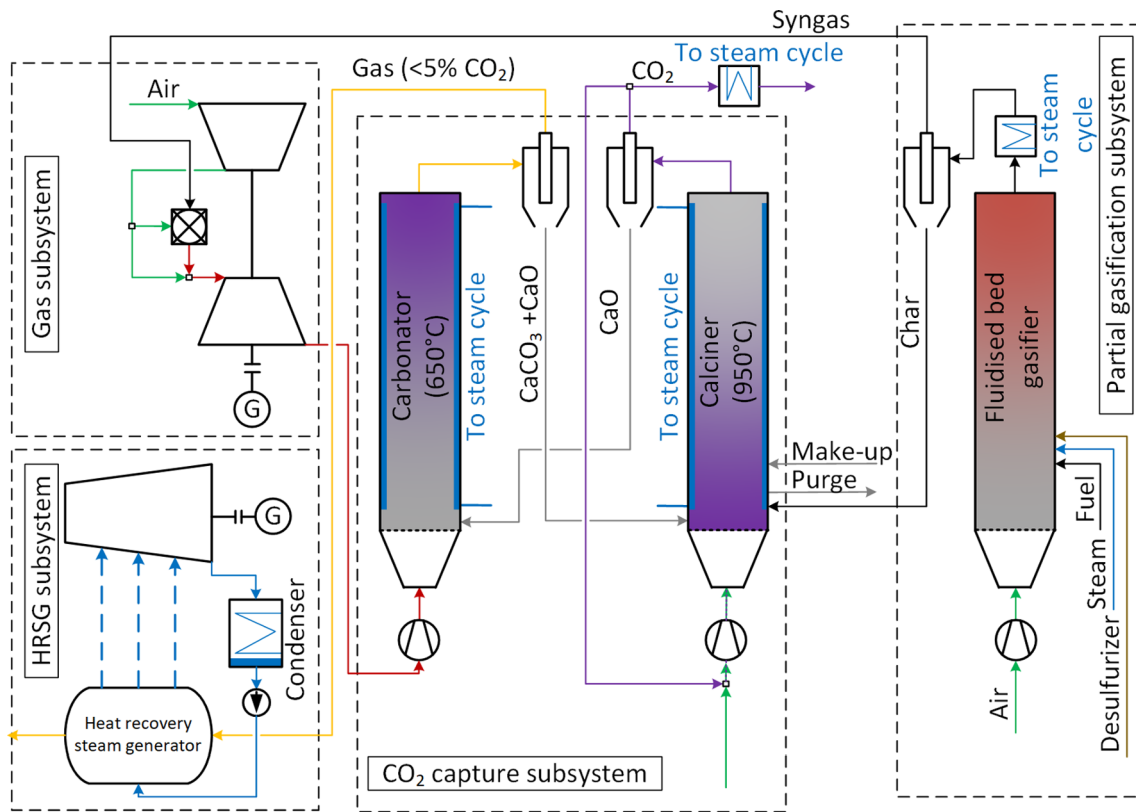


Fig. 11. Main components of the integrated gasification combined cycle power plant with carbonate looping for CO₂ capture (Adapted with permission from Li et al. [101]. Copyright 2011 Wiley.).

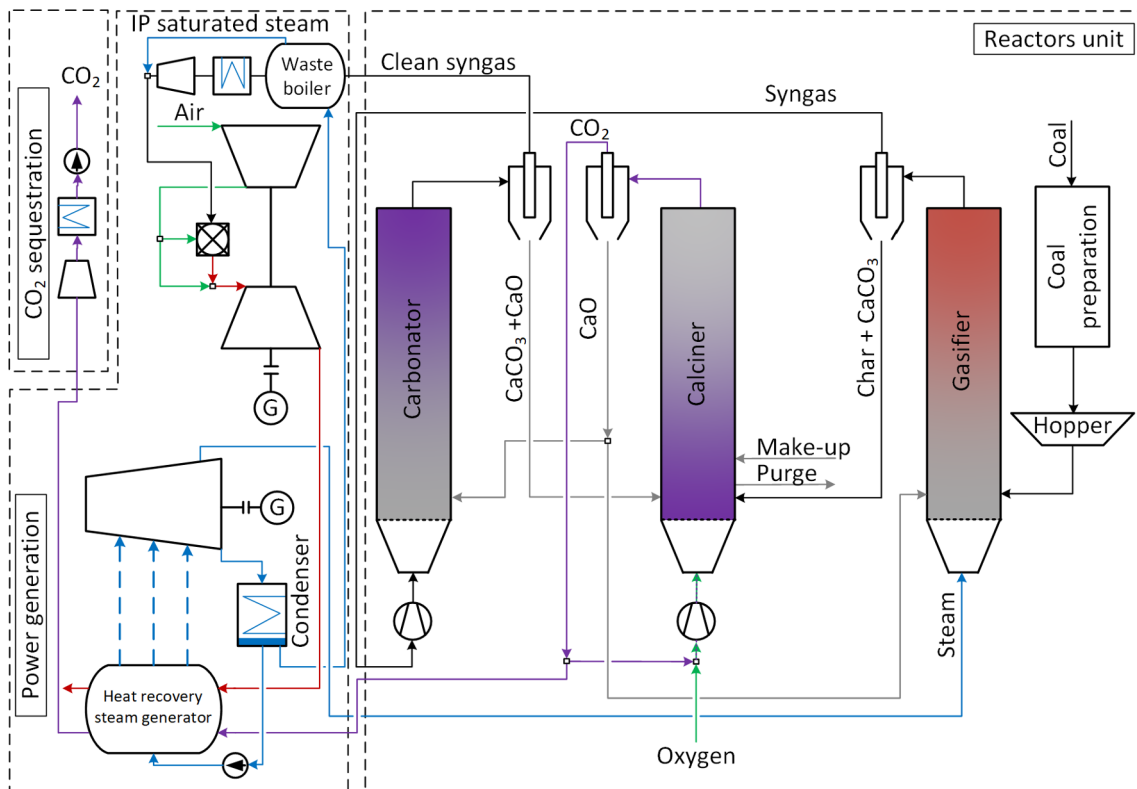


Fig. 12. Conceptual design of integration of carbonate looping plant to integrated-gasification combined cycle power plant (Adapted with permission from Wang et al. [105]. Copyright 2013 Elsevier.).

sub-critical steam cycle. The thermodynamic performance of this hydrogen-fueled IGCC power plant was characterised with a net efficiency between 41.0 and 45.4%, depending on the coal conversion in the

gasifier and the turbine inlet conditions, and a CO₂ capture level of 95%. This was found to be superior to conventional IGCC systems and supercritical CFPPs retrofitted with the ammonia-based CO₂ capture

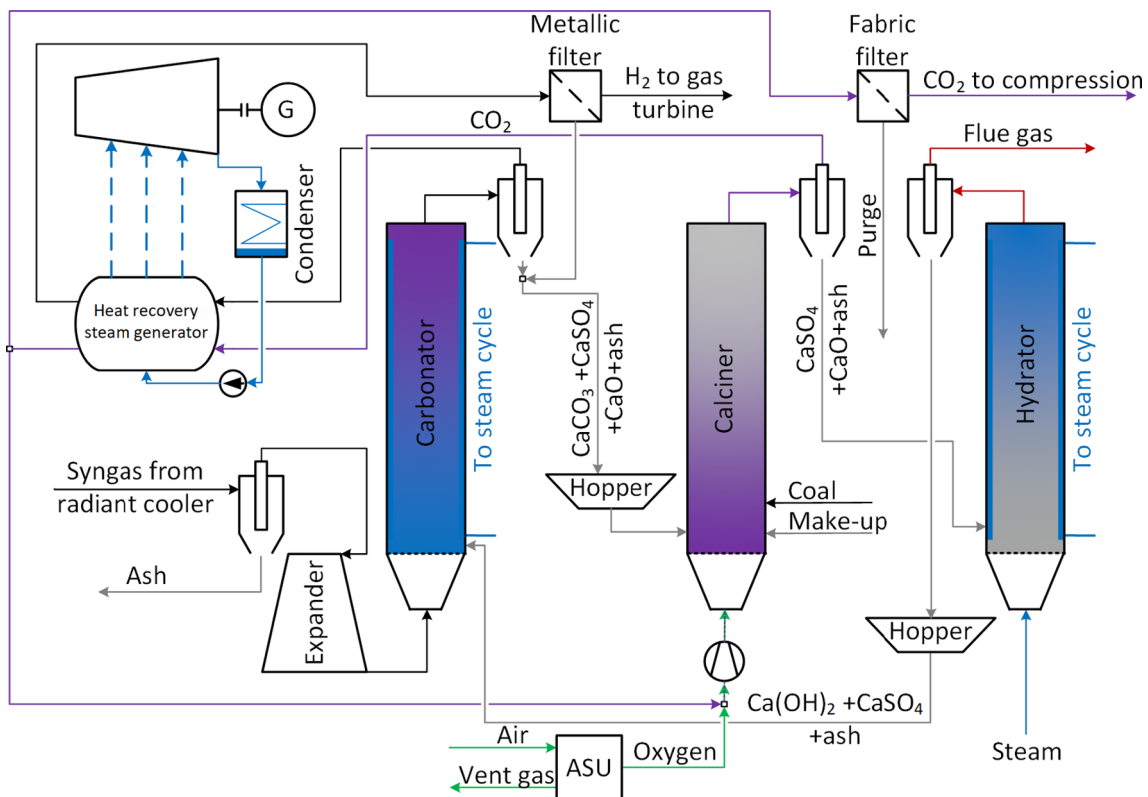


Fig. 13. Conceptual design of integration of carbonate looping plant to integrated-gasification combined cycle power plant (Adapted with permission from Connell et al. [109]. Copyright 2013 Elsevier.).

process that were characterised with net efficiencies of 36.3–38.8% [106,107] and 27.9% [76], respectively.

In contrast to the IGCC concepts that employ steam gasification of coal, Zhu et al. [108] evaluated the feasibility of implementing CaL into an IGCC in which high-purity oxygen was used as the gasifying medium, in addition to steam. Produced syngas was expanded prior to being fed to the carbonator for water-gas shift and CO₂ removal, which took place at an atmospheric pressure. The high-purity hydrogen stream was then utilised in the gas turbine, along with the high-purity nitrogen (N₂) stream from the ASU to lower the combustion temperature and increase the gas flow through the gas turbine. Importantly, an additional amount of coal was oxy-combusted in the calciner for sorbent regeneration. The high-grade heat in the system was then utilised in a sub-critical steam cycle for power generation. The thermodynamic assessment performed by Zhu et al. [108] estimated the net efficiency of the system to be 37.7%, with nearly complete CO₂ removal from the syngas stream. This compares favourably to the physical solvent scrubbing system that, when integrated with the same IGCC, yielded a net efficiency of 36.6%. Nevertheless, CaL was shown to reduce the net efficiency of the conventional IGCC without CO₂ capture by 6.4% points. It needs to be highlighted that the specific capital cost for the IGCC power plant with CaL was estimated to be 1911 €/kW_{el, gross}, which was 14% higher than that of the conventional IGCC without CO₂ capture. Importantly, the specific capital cost of the IGCC with physical solvent scrubbing was 3% higher than that of the corresponding system with CaL, further proving the feasibility of that technology. Similar conclusions were drawn by Connell et al. [109], who evaluated the techno-economic performance of an hydrogen-fueled IGCC that comprised two F-class turbines and a sub-critical steam cycle for high-grade heat recovery. However, as opposed to the previous studies, Connell et al. [109] considered a double-looping CaL that comprised a hydrator operating at 2 bar and 493 °C for sorbent reactivation (Fig. 13). This configuration has been developed and successfully demonstrated at pilot-plant scale by Wang et al. [34,35]. Moreover, both oxy-fired gasifier and carbonator were operated at elevated pressure (56 and 33 bar,

respectively). This required a carbonator temperature of 700 °C to allow calcium hydroxide (Ca(OH)₂) decomposition and, hence, the water-gas shift reaction. Following the state-of-the-art process, the sorbent was regenerated under atmospheric pressure and an operating temperature of more than 875 °C was maintained through oxy-combustion of coal in the calciner. This study has indicated that CaL with hydration would result in a net efficiency of the IGCC power plant of 33.1%, 0.4% points higher than that of the IGCC power plant with a dual-stage Selexol process. This performance was 6.5% points higher than for a comparable subcritical CFPP retrofitted with an amine scrubbing system using monoethanolamine [110]. Yet, the steam requirement for the hydration and high-pressure operation of the gasifier and carbonator resulted in lower net efficiency compared to the process considered by Wang et al. [105]. Nevertheless, Connell et al. [109] have estimated the LCOE of the hydrogen-fueled IGCC power plant to be 72.6 €/MW_{el, h}, lower than the 80 €/MW_{el, h} estimate for the IGCC or CFPP utilising chemical solvent scrubbing for CO₂ capture. Moreover, the specific capital cost of this system (2315.2 €/kW_{el}) was shown to be lower, by 13% and 20%, than that of the IGCC or CFPP utilising chemical solvent scrubbing for CO₂ capture, respectively. This further proves the techno-economic feasibility of CaL in IGCC power plants.

As has been identified above, the main source of parasitic load in CaL stems from oxygen production in the energy-intensive and expensive cryogenic ASU, to enable oxy-fuel combustion in the calciner. To further improve the performance of the hydrogen-fueled IGCC, Kunze et al. [111] proposed substituting the cryogenic ASU with an oxygen-transfer membrane, which utilises highly selective ionic membrane for air separation at high temperatures (850–900 °C). It utilises part of the high-pressure air diverted from the gas turbine compressor, which is mixed with the CO₂ stream fed to the calciner to control its temperature (Fig. 14). Importantly, no additional fuel is utilised in CaL, as the heat requirement for sorbent regeneration in the calciner was met by oxy-combustion of some of the syngas, while the remaining is utilised in the gas turbine. Also, as opposed to the previous hydrogen-fueled IGCC power plant configurations, the high-grade heat is utilised

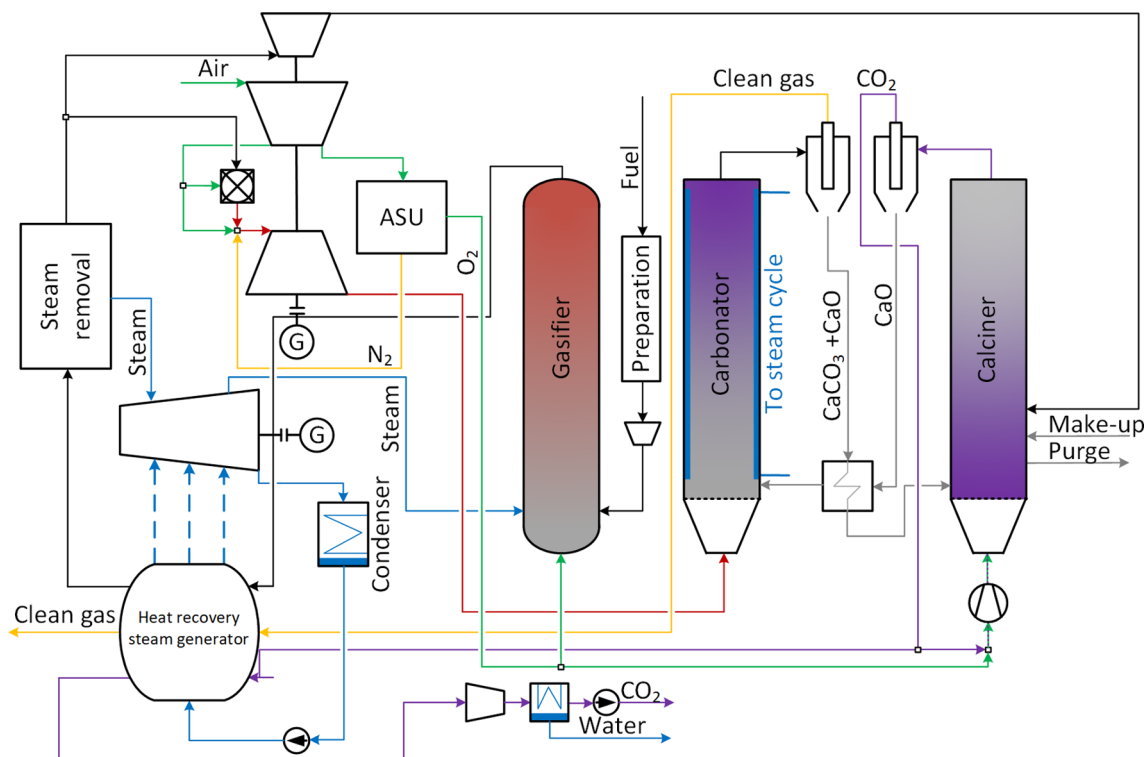


Fig. 14. Conceptual design of integration of carbonate looping plant to integrated-gasification combined cycle power plant (Adapted with permission from Kunze et al. [111]. Copyright 2011 Elsevier.).

in a supercritical steam cycle for power generation. From the thermodynamic perspective, implementation of CaL and an oxygen-transfer membrane resulted in a net efficiency of 43.2%. This was found to be 3.8% points higher than that of conventional IGCC with an acid-gas removal system. It needs to be highlighted that such net efficiencies were in the range for the supercritical CFPPs without CO₂ capture [112,113]. For this reason, IGCC plants with CaL could be a feasible option for low-carbon power generation from coal that will be characterised by higher reliability compared the conventional IGCC due to the lack of a complicated chemical island.

As has been identified in Section 3, use of alternative sorbents may improve the performance of CaL-based systems [34,35,46,66]. Chi et al. [114] evaluated the effect of using CaO and sodium carbonate promoted magnesium oxide (Na₂CO₃-MgO) sorbent on the thermodynamic performance of a number of IGCC power plant configurations. The gasification island considered an oxygen-blown transport gasifier for syngas production, with the high-purity oxygen stream from a cryogenic ASU. The quality of syngas was further improved by considering either conventional two-stage water-gas shift, in which case CaL was located right after the shift reactors, or the sorption-enhanced water-gas shift (SEWGS) process. The cleaned syngas was then utilised in an F-class gas turbine and the high-grade heat utilised in a sub-critical steam cycle. In addition, similarly to the concept evaluated by Kunze et al. [111], part of the syngas stream was oxy-combusted in the calciner for sorbent regeneration. The thermodynamic assessment indicated that, if the conventional two-stage water-gas shift process was employed, the net efficiency of the IGCC with CaL was 36.7% and 37.5% if Na₂CO₃-MgO and CaO were used as a sorbent, respectively. The net efficiency in both cases was increased to 37.3% and 38.1%, if the SEWGS was considered. Poorer performance of the system using Na₂CO₃-MgO was primarily associated with lower temperature in the carbonator (400 °C) and the calciner (680 °C) for that sorbent. This led to less high-grade heat for recovery, and thus less additional power generated. Moreover,

the specific heat requirement for Na₂CO₃-MgO sorbent regeneration was found to be higher than that for CaO sorbent for sorbent conversions below 53%. As the conversions in CaL can vary between 15% [31] and 35% [46], depending on the sorbent degradation and fresh sorbent make-up rate, and considering the fact that the cost of MgO is one order of magnitude higher than that of CaO [115], use of that sorbent cannot be regarded as either technically or economically substantiated.

Another option to improve the performance of the novel gasification-based systems would be to consider alternative power islands that would be characterised with higher efficiencies. Romano and Lozza [116,117] have evaluated the thermodynamic performance of IGCC concepts that utilise CaL both as a pre-combustion CO₂ capture technology and as a heat source for power generation. Both zero-emissions coal mixed technology (ZECOMIX) [117] (Fig. 15) and zero-emissions coal mixed technology with air gas turbine (ZECOMAG) [116] (Fig. 16) can be divided into four sections – chemical island, oxygen island, CO₂ island and power island – and they only differ in the power island configuration. In the chemical island coal slurry is gasified under a hydrogen atmosphere in a hydrogasifier producing syngas that is then shifted to the hydrogen-rich stream in the carbonator. A small amount of oxygen is utilised to sustain the desired operating temperature at 700–1000 °C, depending on the operating pressure, ranging between 30 bar and 70 bar. A fraction of the hydrogen-rich stream is recycled from the carbonator to the hydrogasifier. The power island of ZECOMIX technology comprises a semi-closed Joule cycle, in which flue gas from the syngas oxy-combustion and the combustion gases are mixed with compressed steam to control the combustor outlet temperature. This mixture is expanded in a high-temperature steam turbine and then used for supercritical steam generation in the bottoming steam cycle [117]. Conversely, ZECOMAG technology has a more conventional power island, in which the syngas is burned with air in an open gas turbine cycle, and the discharged flue gas is used to generate supercritical steam in the dual-pressure heat recovery steam generator for the steam

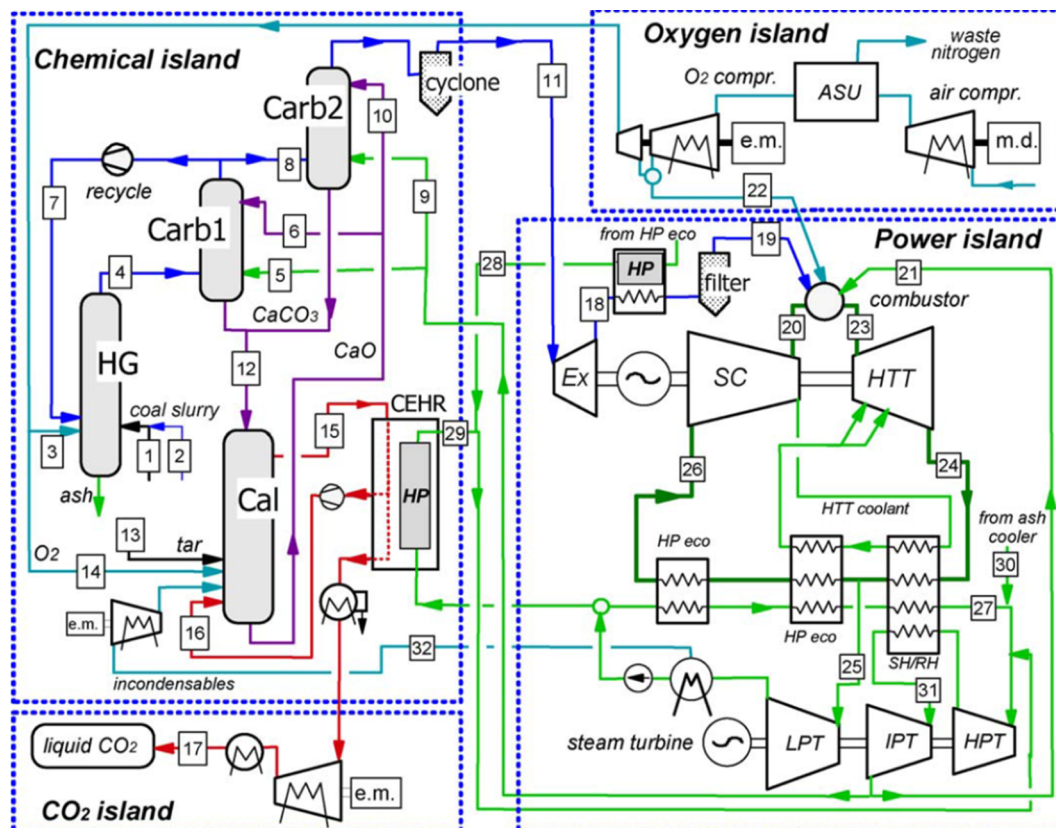


Fig. 15. Conceptual design of Zero-Emissions COal MIXed technology (Reprinted with permission from Romano and Lozza [117]. Copyright 2010 Elsevier.)

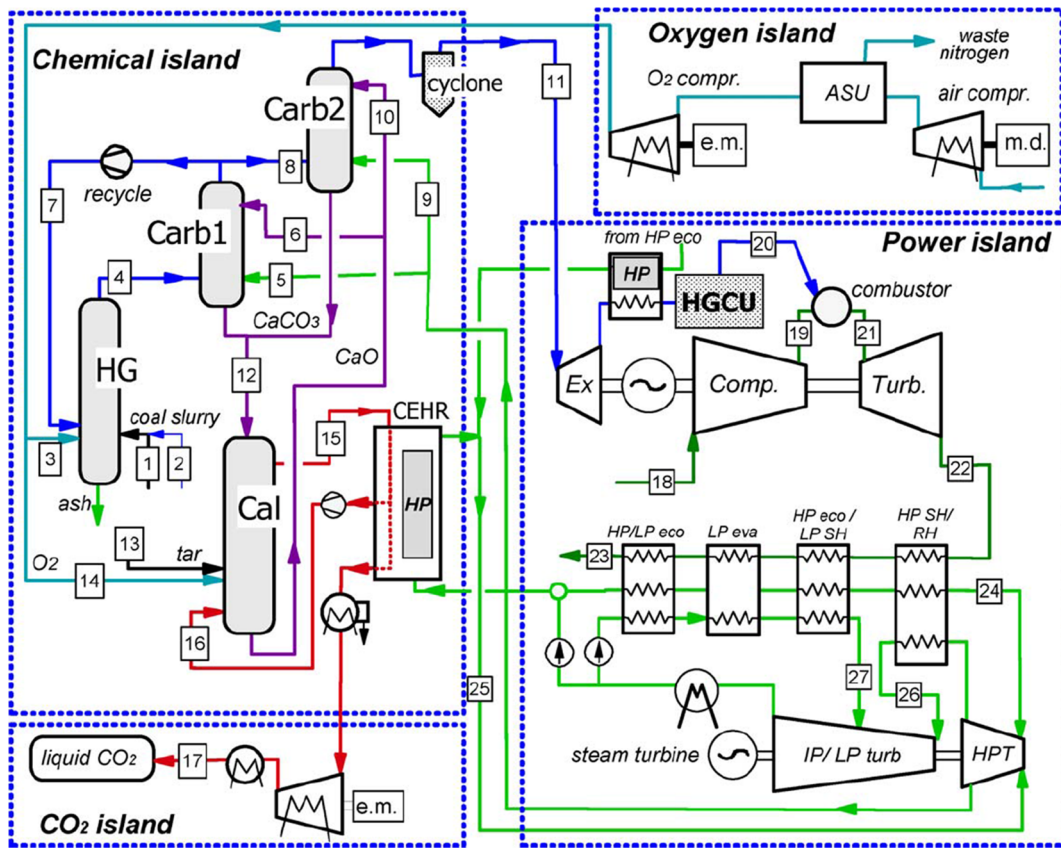


Fig. 16. Conceptual design of Zero-Emissions COal Mixed technology with Air Gas turbine (Reprinted with permission from Romano and Lozza [116]. Copyright 2010 Elsevier.)

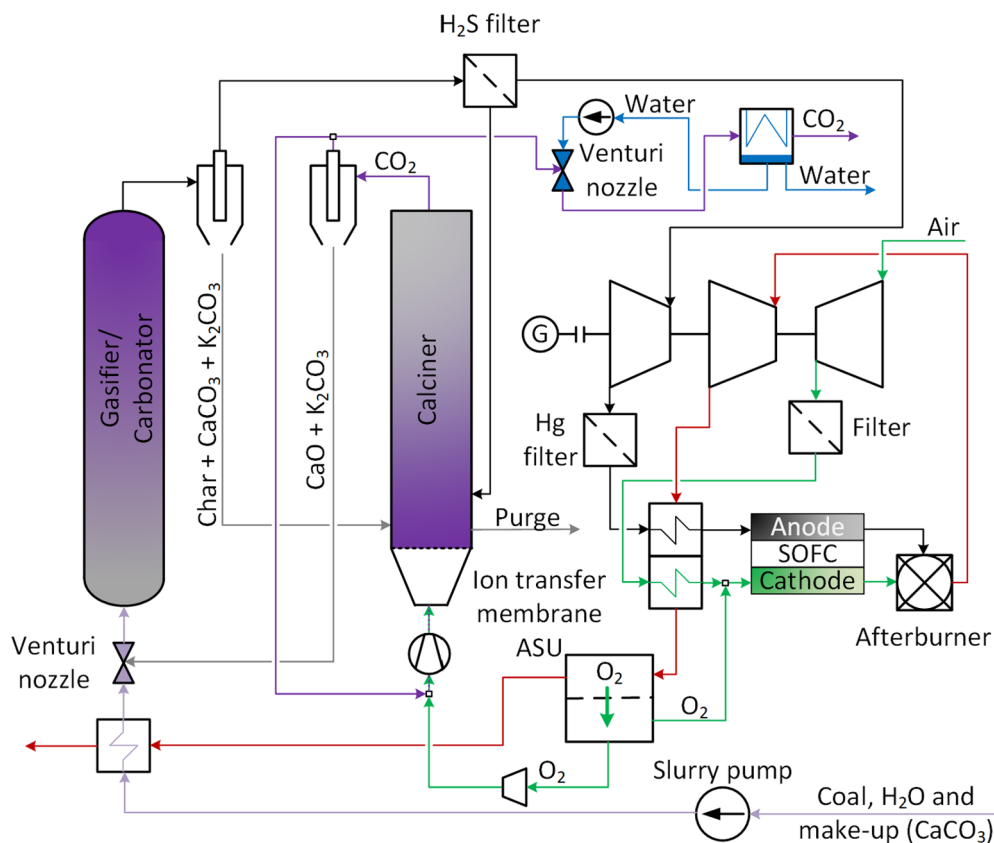


Fig. 17. Conceptual design of integrated-gasification fuel cell power plant (Adapted with permission from Siefert et al. [118]. Copyright 2014 Elsevier.)

cycle [116]. Despite its more conventional configuration, ZECOMAG cannot be considered as a zero-emissions technology as the gas turbine flue gas, which consists of CO_2 , nitrogen oxides (NO_x) and sulphur oxides (SO_x), is exhausted to the environment. Analysis of the overall process performance revealed that both ZECOMIX and ZECOMAG yield net efficiency of 46.7%. The analysis also revealed that the net efficiency of ZECOMIX was degraded by 0.6% point on increase of the steam compressor pressure from 25 bar to 48.5 bar, and by 2.3% points on reduction of the calciner temperature to 920 °C. In addition, reduction of the average sorbent conversion in the carbonator from 66.7% to 20.0% was found to reduce the net thermal efficiency of ZECOMIX by 3% points and of ZECOMAG by 2.5%. This indicates that sorbent performance is critical in terms of the overall process efficiency.

To further improve the performance of the gasification-based systems, Siefert et al. [118] proposed utilising the syngas from sorption-enhanced coal gasification in a solid-oxide fuel cell (SOFC) (Fig. 17). In this integrated gasification-fuel cell (IGFC) power plant, only 76% of the coal was converted to syngas, while the remaining part was oxy-combusted in the calciner. Importantly, although the hydrogen sulphide (H_2S) and carbonyl sulphide (COS) were almost completely captured in CaL, a small amount was still expected to be present in the syngas that could degrade the SOFC. Hence, the H_2S filter, which can be achieved by zinc oxide (ZnO), was considered to remove the H_2S content to less than 1 ppm. This study also compared the techno-economic performance of such a system with that of the IGCC with CaL, which was similar to that described by Kunze et al. [111]. The thermodynamic assessment indicated that the novel process can achieve a net efficiency of 60.2%, which is significantly higher than the 46.4% and 43.2% for the IGCC with CaL estimated by Siefert et al. [118] and Kunze et al. [111], respectively. Nevertheless, the capital cost for the IGFC with CaL was 1600 €/kW_{el, gross}, which was comparable to that of 1520 €/kW_{el, gross} estimated for IGCC with CaL. The latter figure appears to be underestimated compared to the ones reported earlier, that varied between 1800 €/kW_{el, gross} and 2300 €/kW_{el, gross} [102,108,109]. This can be associated with relatively high uncertainty with the equipment cost

estimates, which was reported by Siefert et al. [118] to vary by up to $\pm 40\%$. Nevertheless, utilisation of the SOFC in place of the conventional combination of Brayton and Rankine cycles appears to be a feasible option to improve the techno-economic performance of low-carbon power generation based on CaL.

To further improve the environmental performance of the power generation systems, coal is commonly blended with biomass, which is regarded as a sustainable and carbon neutral fuel [119,120]. Kuo and Wu [121] and Yan and He [122] have evaluated the thermodynamic and environmental performance of an IGFC power plant that produced syngas from blends of coal and biomass. Similar to previous concepts that utilised coal only, the net efficiency of such systems was shown to vary between 44.6 and 50.0%, depending mainly on the coal-to-biomass ratio and location of the CaL unit. Importantly, such a figure is comparable to existing supercritical and ultra-supercritical CFPPs, but it was achieved with significantly reduced specific CO_2 emissions, that can be as low as 10 g CO_2 /kW_{el,h} if CaL was utilised for CO_2 capture after the SOFC [121]. Nevertheless, the economic feasibility of such concepts needs to be proven.

4.3. Sorption-enhanced reforming combined cycle power plants

Building on the legacy of the conventional NGCCs, Zhu et al. [87] proposed a greenfield NGCC that is fed with a mixture of nitrogen from an ASU and high-purity hydrogen produced from the SESR of natural gas that took place subsequently in an oxy-fired reformer and CaL unit (Fig. 18). Importantly, this concept assumed that the heat for sorbent regeneration in the calciner was provided by concentrating solar collectors. As the heat of carbonation reaction was utilised to drive the water-gas shift reaction to obtain high-purity hydrogen, the high-grade heat from the process streams only was utilised in a conventional triple-pressure subcritical steam cycle. Nevertheless, the highest net efficiency of such process was shown to be 46.6%, which was 2.8% points higher than that of the system with separate water-gas shift reactor and CO_2 capture using methyl diethanolamine as a solvent. Moreover, the

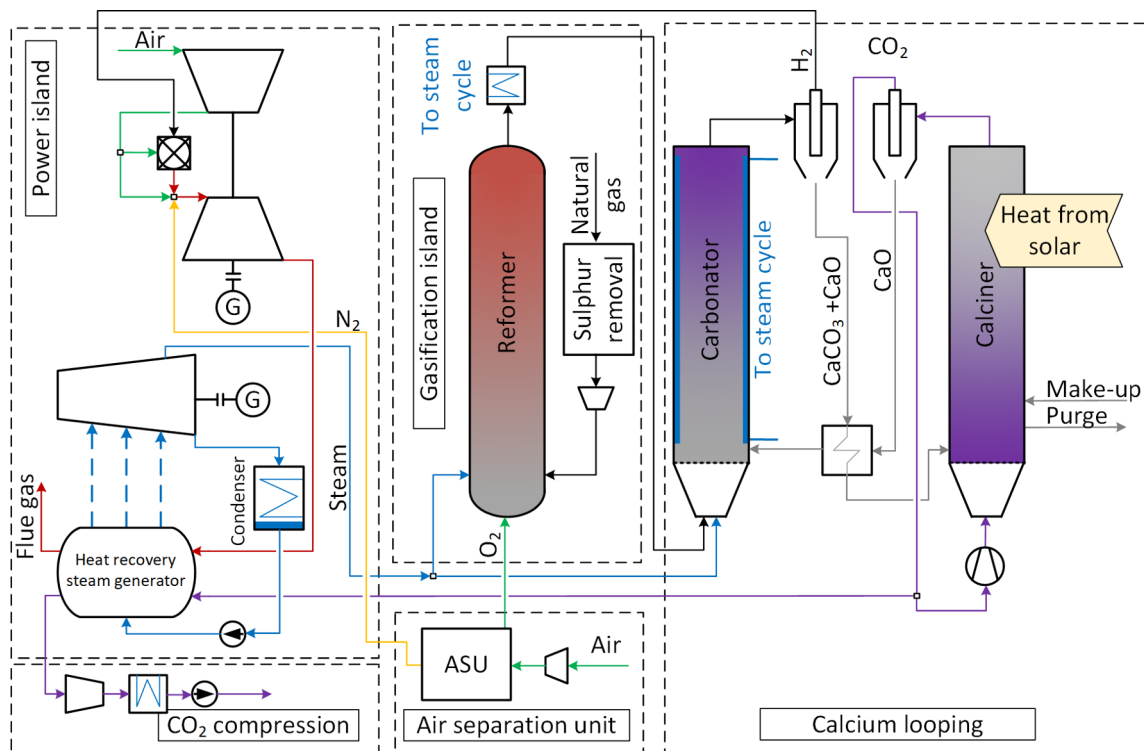


Fig. 18. Concept of combined cycle power plant with sorption-enhanced steam reforming of natural gas (Adapted with permission from Zhu et al. [87]. Copyright 2016 Wiley.).

capital cost of the latter system was shown to be 6% higher than that of the proposed SESR concept, proving the economic feasibility of such concept. Importantly, such techno-economic performance indicated that CaL linked with renewable energy sources has the potential to contribute towards decarbonisation of fossil fuel-fired power generation systems. A similar concept was evaluated by Martinez et al. [90] who proposed to use a calcium-copper chemical looping process for hydrogen production in the combined cycle gas turbine power plant. The hydrogen production island comprises a number of fixed-bed reactors that change their operating conditions to carry out the overall conversion of natural gas to high-purity hydrogen. First, the natural gas is reformed in the presence of steam, the water-gas shift reaction takes place to convert CO to CO₂, and the carbonation reaction occurs to remove CO₂ from the product gas, yielding a high-purity hydrogen stream (50–65%_{vol}). Second, diluted air is fed to the reactor to oxidise copper (Cu) to copper oxide (CuO), so that heat for calcination of CaCO₃ formed in the previous stage is provided. Third, the reduction of CuO with the gaseous fuel, such as natural gas, CO or hydrogen, takes place and, as that reaction is also exothermic, the calcination process is completed. The high-purity hydrogen produced in the calcium-copper chemical looping process is fed to the gas turbine and the high-grade heat from process streams is utilised for power generation in the triple-pressure subcritical steam cycle. Assessment of the thermodynamic performance of the integrated combined cycle with calcium-copper chemical looping revealed that the net efficiency would be between 48.9% and 50.9%. This was shown to be 9.9% points and 7.9% points, respectively, lower compared to the conventional NGCC without CO₂ capture. Such performance falls in the lower range of figures reported for other CO₂ capture technologies in the literature, including the concept of NGCC-SESR linked with concentrating solar collectors evaluated by Zhu et al. [87]. This, in addition to its compact design, indicates that calcium-copper chemical looping can be a feasible option for decarbonisation of the NGCC, if it is proven to be economically competitive to other hydrogen-fired power generation systems.

To further improve the thermodynamic performance of power generation systems using hydrogen, it has been proposed to integrate the SESR process with SOFC that is capable of generating electricity at a high efficiency, up to 70%, especially when linked with another power cycle. Wiranarongkorn et al. [88] have evaluated the process comprising the SESR of bio-oil and the SOFC for power generation (Fig. 19). In this process, the amount of heat generated in the carbonation and water-gas shift reactions was higher than that required by the steam reforming reaction. Therefore, the excess heat is used to preheat the air entering the SOFC. Moreover, it was proposed that the heat for sorbent regeneration in the calciner is indirectly provided from combustion of the unutilised fuel from the SOFC, similarly to the indirect heat transfer concepts proposed previously for post-combustion CaL [36,42,44,45]. The waste heat was utilised to preheat the water and bio-oil streams prior to SESR. This study has indicated that application of SESR using Ca-based sorbent can increase the maximum hydrogen concentration by 45% at lower operating temperature (48.7% at 600 °C), compared to the hydrogen concentration from the conventional steam reforming (33.7% at 700 °C). Hence, no additional water-gas shift reactor is required, and the hydrogen produced in the SESR can be directly used in the SOFC. The performance analysis of the optimal case was characterised with a net efficiency varying between 42.3% and 46.0%, depending on the degree of heat integration. A similar process was evaluated by Diglio et al. [91,123] who proposed integrating CaL with chemical looping for SESR of natural gas with SOFC for power generation. In that process, similar to the calcium-copper chemical looping evaluated by Martinez et al. [90], a high-purity hydrogen stream (92%_{vol}) is produced in a number of fixed bed reactors that are filled with Ni-based catalyst and Ca-based sorbent. It also assumes that the heat requirement of the SESR process is provided by both high-grade heat from the SOFC and combustion of a fraction of the high-purity hydrogen stream. This study indicated that the net efficiency of the

process proposed by Diglio et al. [123] would reach 51%. Importantly, the thermodynamic performance of the processes evaluated by both Diglio et al. [123] and Wiranarongkorn et al. [88] is comparable to the NGCC-SESR concepts evaluated by Zhu et al. [87] and Martinez et al. [90]. The study by Diglio et al. [91] showed that if the integrated CaL with chemical looping was employed for SESR to produce high-purity hydrogen which is then used in SOFC, the LCOE and the cost of CO₂ avoided would be 78 €/MW_{el}h and 36.8 €/tCO₂, respectively. Yet, the LCOE is nearly double that reported for the reference NGCC and higher than that reported for the novel coal-fired power generation concepts. This is primarily because the specific capital cost of the conventional NGCC varies between 550 and 700 €/kW_{el} [81,124] while it is between 1000 and 4000 €/kW_{el} for the SOFC [115,125,126]. Nevertheless, it is expected that a significant cost reduction of the SOFC can be achieved once this technology becomes commercially deployed [127]. Should the capital cost of the SOFC reduce by 50%, the LCOE and the cost of CO₂ avoided would be substantially reduced (48 €/MW_{el}h and 23 €/tCO₂), making such process competitive from both thermodynamic and economic standpoints.

Importantly, the net efficiency of the SOFC-based systems proposed by Diglio et al. [91] and Wiranarongkorn et al. [88] relied solely on the performance of the SOFC itself, with the high-grade heat being utilised within the system. As indicated above, linking SOFC with another power cycle has the potential to significantly increase the net efficiency of the system. In this vein, Wu et al. [86] has proposed a triple combined cycle power plant (Fig. 20) in which the hydrogen-rich fuel from SESR is first partially utilised (~80%) in the SOFC operating at 10 bar. The unutilised fuel is burnt in the afterburner and the high-temperature flue gas is fed to the gas turbine. The waste heat in the flue gas is utilised in a sub-critical steam cycle. As opposed to the other SOFC-SESR systems, the heat for sorbent regeneration is provided by direct oxy-fuel combustion of methane in the calciner. After optimisation of the operating conditions of the proposed process, its net efficiency was estimated to be 60.6%. Such performance is superior to that reported for the NGCC-SESR concepts evaluated by Zhu et al. [87] and Martinez et al. [90], and the SOFC-SESR systems proposed by Diglio et al. [91,123] and Wiranarongkorn et al. [88]. However, the economic feasibility of such process is yet to be proven.

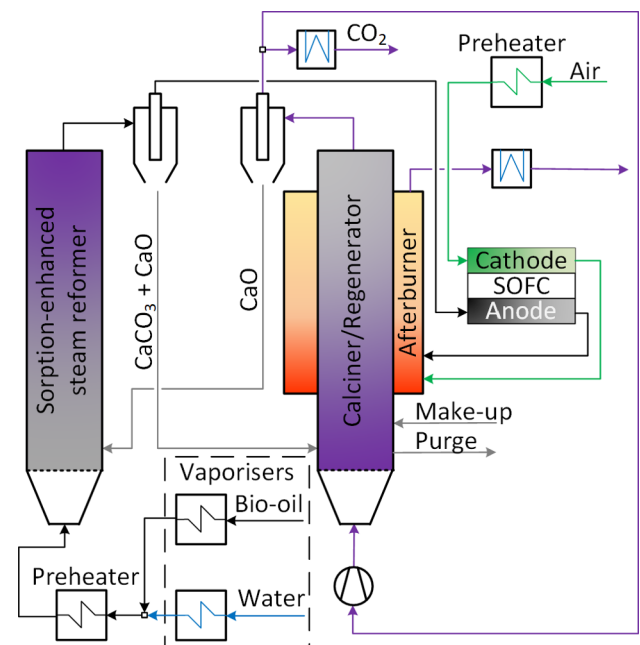


Fig. 19. Concept of solid oxide fuel cell integrated with sorption-enhanced steam reforming of bio-oil (Adapted with permission from Wiranarongkorn et al. [88]. Copyright 2017 Elsevier.).

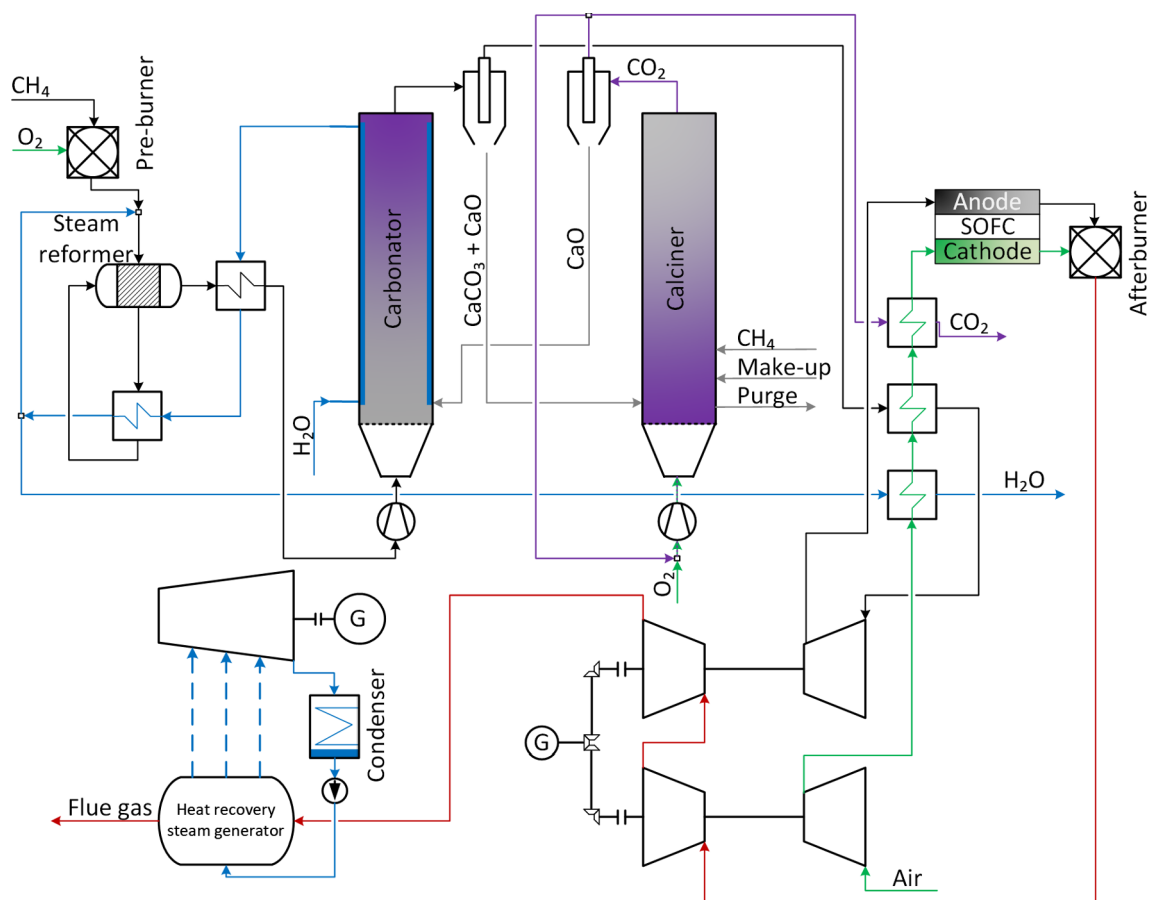


Fig. 20. Concept of triple combined cycle power plant with sorption-enhanced steam reforming of natural gas (Adapted with permission from Wu et al. [86]. Copyright 2017 Elsevier.).

5. Thermodynamic feasibility assessment

In the retrofit scenario, CaL can be implemented in conventional fossil fuel-fired power generation systems as a post-combustion CO₂ capture system. Depending on whether CaL was retrofitted to a CFPP or NGCC, the net efficiency of the system was shown to be between 24 and 44% and 45–53%, respectively. It needs to be highlighted that such figures align well with the ones reported for the unabated CFPPs (27–43%) and NGCCs (43–53%) in the existing fossil fuel-fired power plant fleet [128,129]. Importantly, the existing fleet comprises a large share of subcritical units that operate with net efficiencies lower than 33% [130]. Therefore, implementation of CaL to the state-of-the-art super- and ultra-supercritical units, which can reach 42–50% (CFPP) [131,132] and 43–58% (NGCC) without CO₂ capture [132], may not have a significant effect on the average net efficiency of the power generation fleet. As can be observed in Fig. 21a, net efficiency of the conventional fossil fuel-fired power generation system retrofitted with CaL that was most often reported in the reviewed literature ranges between 30% and 35% (CFPP retrofits), and 45 and 50% (NGCC retrofits). The first range reflects the mode and median figures for the CaL retrofits to the CFPPs that are 33.4% and 32.4%, respectively, while the second reflects the mode and median figures for the CaL retrofits to the NGCCs that are 47.3% and 49.2%. Regardless of better thermodynamic performance reported for NGCC retrofits compared to CFPP retrofits, the former were reported to have a higher impact on the performance of the conventional fossil fuel-fired power generation system (Fig. 21b). Namely, the NGCC retrofits were shown to result in efficiency penalties ranging between 5 and 12.5% points with the mode and median equal to 10% points and 8.5% points. Conversely, CaL retrofits to CFPPs were reported to result in 1.8–14.2% points' decrease in the net efficiency of

the entire system with the mode and median equal to 7.4% points and 6.4% points. In this vein, the current literature indicates that retrofitting CaL to NGCCs is characterised with more technical challenges compared to its retrofit to CFPPs. This can primarily be associated with much lower CO₂ concentration in the flue gas from NGCCs (~4%_{vol}) compared to CFPPs (~15%_{vol}). Therefore, to achieve a CO₂ capture level between 85% and 90% in the carbonator, its operating temperature needs to be reduced to 600 °C in the NGCCs retrofits. Moreover, due to the considerably larger volume of flue gas to be processed, it may need to be preheated depending on whether CaL is located downstream or upstream of the primary steam cycle in NGCCs [84]. Regardless of the less favourable conditions for CO₂ capture compared to CFPPs, several modifications presented in Section 3, including improved heat integration, exhaust gas recirculation, utilisation of different sorbents and utilisation of higher-efficiency power cycles to use the high-grade heat from CaL, can improve the thermodynamic performance of the CaL retrofitted to an NGCC. Fig. 21b reveals that the set of values for the efficiency penalty associated with the CaL retrofit that occur most often in the existing literature were within the range between 6 and 8% points. However, substantial potential exists to reduce the efficiency penalty below 5% points on utilisation of alternative process configurations, including the use of alternative power cycles for high-grade heat recovery from CaL, and sorbents, as indicated in Section 3. It needs to be highlighted, however, that the thermodynamic performance of the CaL retrofits reported in the current literature compares favourably to both oxy-combustion and chemical solvent scrubbing technologies [133,134], as these have been predicted to result in efficiency penalties ranging between 7 and 13% points [6,7].

In the greenfield scenario, CaL has been used as a base technology to develop novel power generation systems that are characterised with

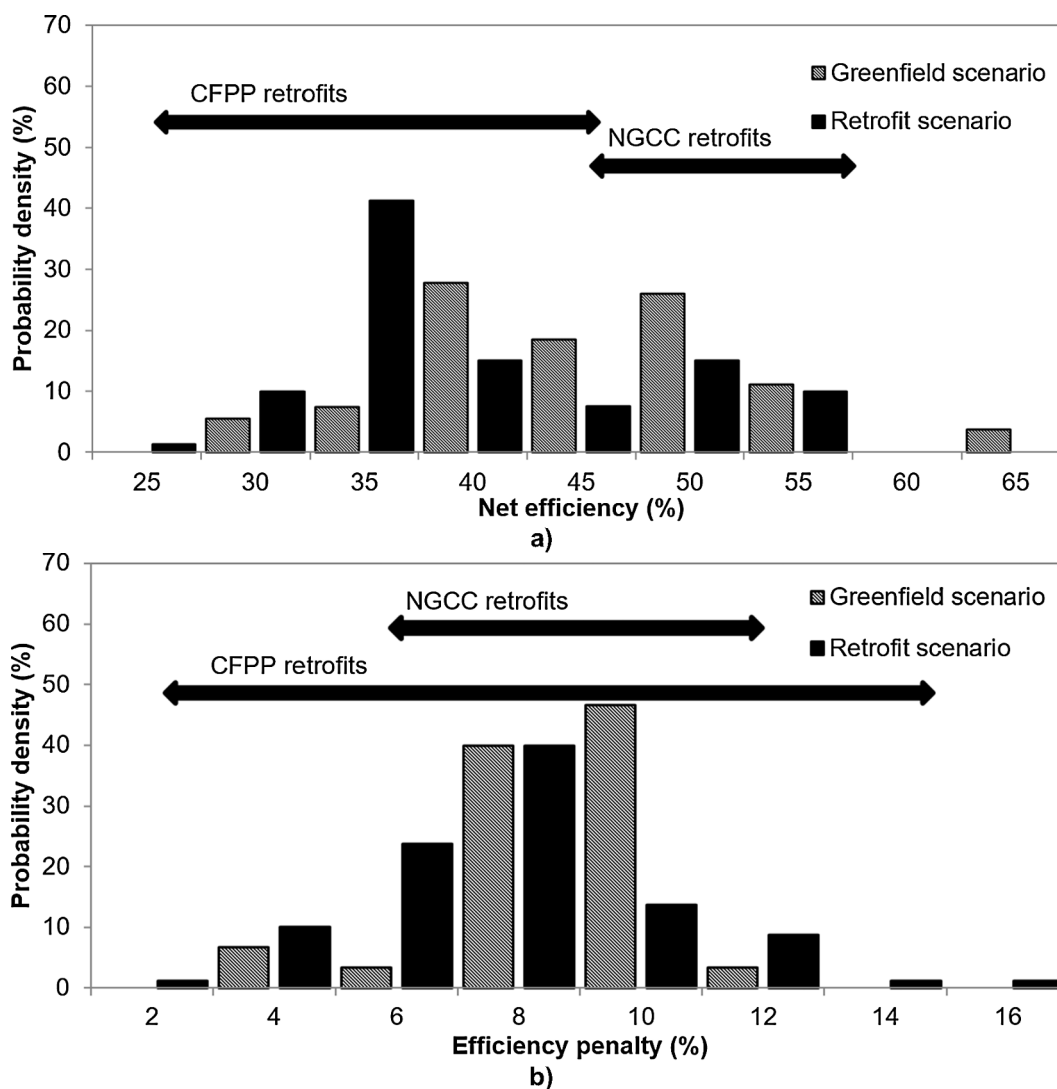


Fig. 21. Distribution of the (a) net efficiency and (b) efficiency penalty in the reviewed carbonate looping concepts.

high-efficiency and low CO₂ emissions. These have been classified as combustion-, gasification-, and reforming-based systems that were reported to achieve net efficiencies ranging between 28.6 and 60.6% with the mode and median equal to 51% and 42.6%, respectively (Fig. 21a). This indicates that such concepts may achieve higher net efficiencies than NGCCs (34–53%) in the existing fossil fuel-fired power plant fleet [128,129], but at considerably smaller environmental impact. Depending on the type of fuel used in the system and its thermochemical conversion technology, the most often-reported net efficiency of greenfield power generation systems ranges between 35% and 40% (CaL-based CFPPs), and 45% and 50% (integrated gasification and sorption-enhanced reforming-based power plants). The CaL-based CFPPs based on hybridising oxy-combustion with CaL were shown to result in net efficiencies of 28.6–37.4% with efficiency penalties between 7 and 9.2% points. Such performance is comparable to the CFPP retrofit scenarios reviewed in Section 3.1. The main benefit of such hybrid concepts, however, is the higher CO₂ capture level that can reach close to 99%. Conversely, the concepts based on the CaL process were reported to reach net efficiencies of 34.9–40.2% and result in efficiency penalties of 2.4–4.4% points. As the performance of these concepts can be further improved utilising the measures reported in Section 3, such as increase in the degree of heat integration or utilisation of higher-efficiency power cycles, the CaL-based CFPPs can be seen as feasible options to replace the existing unabated CFPPs in the mid-

term. The CaL-based IGCCs, in which coal or biomass is first converted into syngas and then utilised in the combined cycle, were reported to achieve net efficiencies ranging between 33.1 and 60.2%. The information on the efficiency penalty was found to be limited, as it was only reported by Cormos and Cormos [104], Cormos [102], and Chi et al. [114]. These studies indicated that the net efficiency of CaL-based IGCCs would be lower by 6.4–10.2% than the corresponding efficiency of conventional IGCCs. Nevertheless, most of the concepts presented in the current literature were reported to result in net efficiencies higher than 40%. Importantly, where the IGCC included the SOFC in addition to the gas turbine, the net efficiency was reported to be between 46.4 and 60.2%, even if biomass was used in syngas production. Such net efficiencies are considerably higher compared to those reported for novel combustion-based CFPPs in Section 4.1 (28.6–40.2%) and for existing unabated CFPPs (27–43%) reported in the literature [128,129]. Importantly, the IGCC concept utilising SOFC may even result in higher net efficiencies than those of the existing unabated NGCCs (34–53%). The CaL-based SESR concepts, in which natural gas was reformed into high-purity hydrogen and then utilised in a gas turbine and/or SOFC, were reported to achieve similar performance to CaL-based IGCCs, as their net efficiencies were reported to be between 42.3 and 60.2%. A study by Martinez et al. [90] compared the thermodynamic performance of CaL-based NGCC-SESR with the conventional NGCC without CO₂ capture, and indicated that the net efficiency of such a novel

concept would vary between 48.9 and 51.0%, resulting in an efficiency penalty ranging between 7.8 and 9.9%. Although the CaL-based SESR concepts produce high-purity hydrogen, linking them with standalone SOFCs was shown to yield net efficiencies of 42.3–51%. This is at best comparable to the CaL-based NGCC-SESR concepts that utilise conventional NGCC architecture. Importantly, the CaL-based SESR concepts that combine SOFC with another power cycle were shown to achieve a net efficiency of 60.2%. It needs to be highlighted that in contrast to the CaL-based IGCCs, all proposed CaL-based SESR concepts result in net efficiencies higher than 40%, and most of them achieve net efficiencies around 45–50% with the potential to reach 60%. Such figures are comparable to those reported for existing unabated NGCCs (43–58%) [132], indicating that CaL-based SESR concepts could offer comparable thermodynamic performance to existing systems, but at a much lower environmental impact. Overall, it can be noted that the net efficiencies reported for the greenfield scenarios are higher compared to those for the retrofit scenarios. This indicates that the CaL-based power generation systems could be implemented in place of the existing fleet of conventional fossil fuel power plants, leading to both increased average net fleet efficiency and substantial reduction in its carbon intensity.

6. Economic feasibility assessment

As opposed to the thermodynamic feasibility assessments, the data supporting the economic feasibility of the CaL concepts appears to be limited in the current literature, especially for the greenfield scenarios. Therefore, the thermodynamic feasibility of the CaL-based power generation systems still needs to be substantiated via their economic feasibility.

The current literature most often report that retrofit of CaL to fossil fuel-fired power generation systems will result in LCOEs between 50 and 75 €/MWh (Fig. 22a), and the cost of CO₂ avoided (AC) was most often reported to be between 10 and 30 €/tCO₂ (Fig. 22b), regardless of whether CaL was retrofitted to NGCC or CFPP. Such economic performance has been shown to be superior to chemical solvent scrubbing (LCOE = 65–89 €/MWh; AC = 35–75 €/tCO₂) [73,75–78] and oxy-fuel combustion (LCOE = 55–75 €/MWh; AC = 35–75 €/tCO₂) [135,136] retrofits.

As indicated above, a limited amount of data have been presented in the current literature on the economic performance of CaL-based power generation systems. These data indicate that the LCOE and the cost of CO₂ avoided associated with the greenfield scenarios are most likely to be within 50–100 €/MWh and 10–50 €/tCO₂, respectively (Fig. 22).

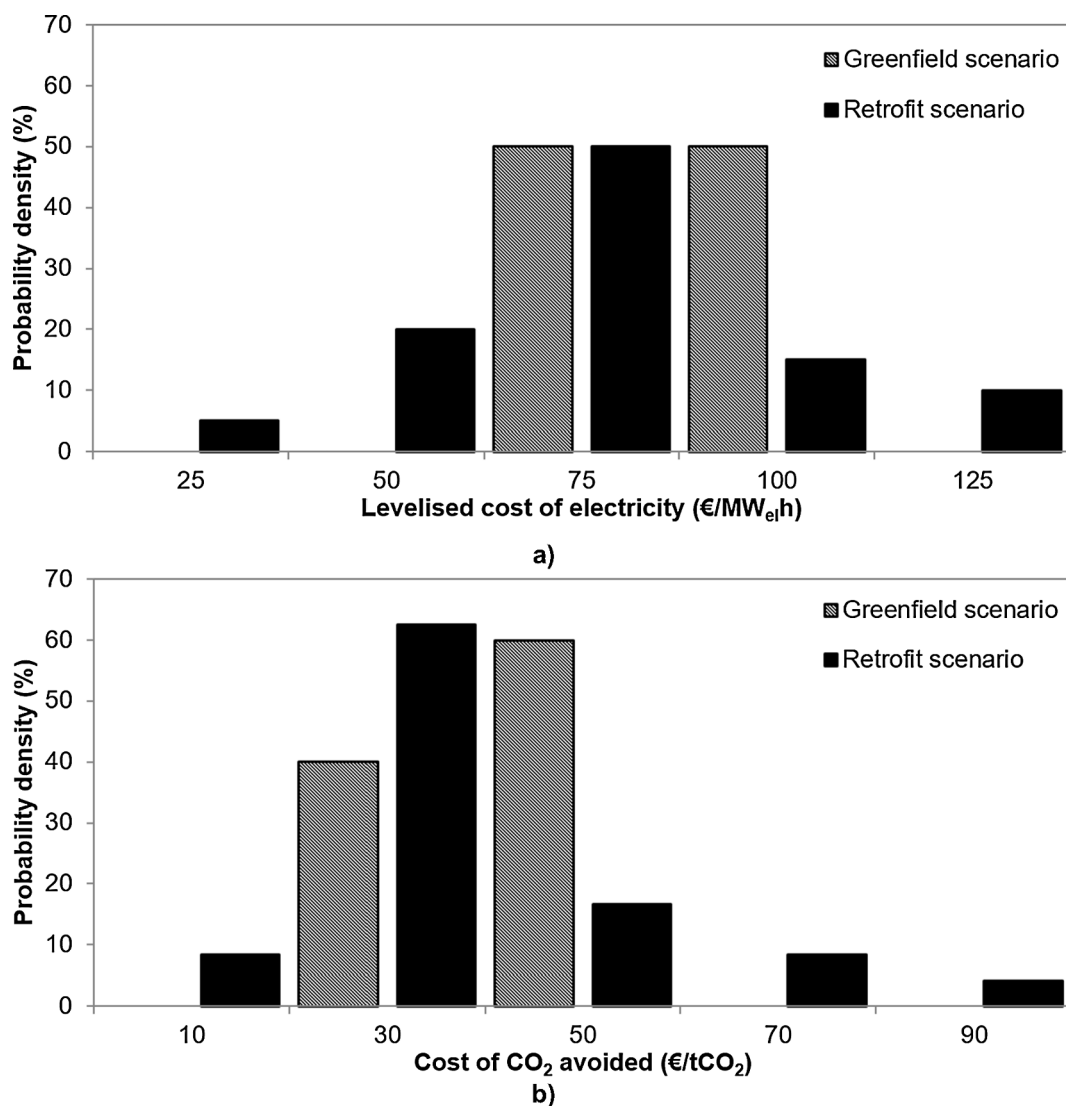


Fig. 22. Distribution of the (a) levelised cost of electricity, (b) cost of CO₂ avoided in the reviewed carbonate looping concepts.

Although such economic performance appears to be competitive to that reported for the retrofit scenarios, economic feasibility of such novel concepts must be further proven to substantiate their competitive thermodynamic performance assessed in Section 5. It also needs to be highlighted that, although alternative sorbents may be characterised with lower degradation than natural sorbents, their high price may make them not economically feasible [68]. Therefore, it is pertinent that the optimisation and development of CaL-based power generation systems are supported by both thermodynamic and economic feasibility assessment. Finally, the economic assessments presented in the current literature are mostly based on deterministic models that do not account for the uncertainty in the operating conditions of CaL and the market conditions. As indicated by Hanak and Manovic [69], the most probable values of the LCOE in the CaL retrofit to CFPPs will be between 75 and 115 €/MWh. As this range is higher than that identified using the deterministic models, it is pertinent to consider the effect of uncertainty on the economic performance.

7. Perspective for carbonate looping cycles

Timely decarbonisation of the power sector is crucial to meeting a challenging emission reduction target set out by the Paris Agreement. Such transformation of this sector can only be achieved via wide implementation of low-carbon power generation concepts, including novel power generation systems with CCS. However, the most mature technologies, such as chemical solvent scrubbing and oxy-combustion, impose a significant thermodynamic and economic burden on retrofitting to existing fossil fuel-fired power generation systems. CaL has been shown to be a feasible technology that, when optimised, has the potential to ensure low-carbon power generation at an affordable cost.

The current literature presents a wide number of CaL concepts for decarbonisation of fossil fuel-fired power generation systems that can be broadly classified into retrofit and greenfield scenarios. Retrofits of CaL concepts to existing fossil fuel-fired power plants have been shown to result in efficiency penalties between 6 and 8% points, with net efficiencies varying between 24 and 44% for CFPP and 45–53% for NGCC retrofits. However, considering a large number of alternative CaL configurations and more stable sorbents, the potential exists to reduce the efficiency penalty to below 5% points. This would not only lead to improved economic performance of the entire system, but also to reduced GHG emissions over its lifetime. Furthermore, the CaL-based power generation systems have been shown to be most likely to achieve net efficiencies as high as 40% for CaL-based CFPPs and 50% for CaL-based IGCC and SESR power plants. Yet, similarly to the retrofit scenarios, there is still the potential for further improvement of their thermodynamic performance via increased degree of heat integration and/or utilisation of higher efficiency power cycles. Overall, the net efficiencies reported for the greenfield scenarios are higher than for the retrofit scenarios. Therefore, CaL-based power generation systems could be implemented in place of the existing fleet of conventional fossil fuel power plants, which contains a large share of subcritical CFPPs characterised with net efficiencies lower than 33%, resulting in both increased average net fleet efficiency and substantial reduction in the carbon intensity.

Importantly, the current literature presents limited information on the economic feasibility assessment of CaL concepts, especially for the greenfield scenarios. The cost of CO₂ avoided has been shown to be between 10 and 30 €/tCO₂ and 10–50 €/tCO₂ in the retrofit and greenfield scenarios, respectively. Such economic performance has been shown to be superior to that of chemical solvent scrubbing (AC = 35–75 €/tCO₂) and oxy-fuel combustion (AC = 35–75 €/tCO₂) retrofits, as the costs associated with CO₂ capture using CaL were shown to be nearly half that of mature CCS technologies.

Nevertheless, a vast majority of the assessments of the CaL-based power generation systems included only thermodynamic analyses, and lacked any indication about potential improvements to the economic

performance. It needs to be stressed that the improvements in the thermodynamic performance of such processes, achieved as a result of novel process configuration development and application of more durable sorbents, needs to be substantiated by the economic analysis. This is particularly important regarding sorbents, as regardless of lower degradation, the novel sorbents may be characterised with a high price making the entire process not economically feasible. Finally, existing assessments of the economic feasibility of CaL concepts are based on deterministic models that do not account for uncertainty in the operating conditions of CaL and the market conditions. To account for uncertainty and increase the reliability of the predictions, it is pertinent to incorporate a stochastic approach into the economic assessment.

Overall, the current reading of CaL-based power generation systems indicates that these have significant potential to achieve net efficiencies above 50%, especially if the process includes SOFC, at near-zero (10 gCO₂/kWh) or negative (biomass-fired systems) CO₂ emissions. Such performance can be seen as competitive to the state-of-the-art NGCCs without CO₂ capture, implying that wide deployment of CaL-based power generation systems, especially IGCCs and SESR-based power plants, would result in decarbonisation of the power sector with no energy penalty. Importantly, the existing fleet comprises a large share of subcritical units that operate with the net efficiencies lower than 33%. Therefore, not only can a substantial reduction in the carbon intensity of the power plant fleet be achieved, but also there is the potential for an improvement in the average net fleet efficiency. It is critical, however, to assess the economic performance of CaL-based power generation systems to substantiate their thermodynamic performance and benchmark their attractiveness to the market.

8. Conclusions

CaL is often regarded as an emerging CO₂ capture technology that can reduce economic and efficiency penalties associated with more mature technologies. Its maturity has increased significantly over the past twenty years, mostly due to development of novel process configurations and sorbents for improved process performance. This review aimed to provide a comprehensive overview of CaL concepts and statistically assess their techno-economic feasibility based on the evidence published in the literature. It has been shown that:

- CaL can both be efficiently retrofitted to existing fossil fuel-fired power generation systems and be the basis for development of novel greenfield power generation systems;
- CaL retrofits have most commonly been reported to result in efficiency penalties between 6 and 8% points when retrofitted to existing fossil fuel-fired power generation systems;
- CaL-based greenfield power generation systems can achieve net efficiencies as high as 40–60% at near-zero CO₂ emissions, especially when sorption-enhanced hydrogen production and SOFC are considered;
- a number of measures for net efficiency improvements have been proposed, including increased degree of heat integration, using advanced power cycles, and advanced CaL configurations;
- the cost of CO₂ avoided associated with CaL is 10–50 €/tCO₂ and is superior to that of chemical solvent scrubbing and oxy-fuel combustion; and
- improvements in thermodynamic performance are not always supported by economic assessments.

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