Hybrid carbon capture systems

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Abstract

In most discussions of systems for capturing CO_2 from coal-fired power plants, three options are described. These are:

- post-combustion capture;
- oxyfuel combustion;
- pre-combustion capture.

Recently, some researchers have realised that it may be possible to pick and choose among the elements of the main CO_2 capture systems and develop hybrid systems which are possibly cheaper and more energy efficient. The systems to be discussed in this brief survey include:

- post-combustion capture with oxygen enriched combustion;
- regenerable sorbents (calcium looping) with oxyfuel combustion;
- post-combustion capture in IGCC plants;
- gasification with oxyfuel;
- gasification with chemical looping.

Most hybrid systems are at a very early stage of development compared with the conventional methods with much of the research aimed at evaluation or modelling.

Acronyms and abbreviations

AR   air reheater
ASU   air separation unit
CCS   carbon capture and storage
CFBC   circulating fluidised bed calciner
CLC   chemical looping combustion
COE   cost of electricity
CRIEPI   Central Research Institute of Electric Power Industry (Japan)
CV   calorific value
FR   fuel reactor
HHV   higher heating value
HRSG   heat recovery steam generator
IGCC   integrated gasification combined cycle
IGCC-CL   IGCC with carbonate looping
IGCC-ITM-CL IGCC with ion transport membrane and carbonate looping
IGSC   integrated gasification steam cycle
MDEA   monodiethanolamine
MEA   monoethanolamine
OTM   oxygen transfer membrane
PSA   pressure swing adsorption
RSC   radiant syngas cooler
SCL   syngas chemical looping
SGR   syngas redox
WGS   water-gas shift

Contents

1   Introduction

In most discussions of systems for capturing CO_2 from coal fired power plants, three options are described. These are:
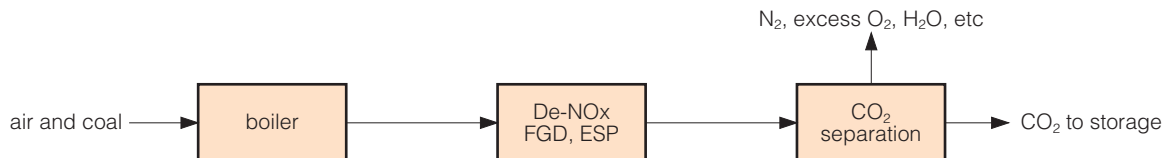
 . post-combustion capture;
 . oxyfuel combustion;
 . pre-combustion capture.

Briefly, post-combustion capture uses chemical solvent sorbents although solid sorbents and membranes have also been studied. Oxyfuel combustion is a process that eliminates nitrogen from the oxidant by burning the fuel in a mixture of oxygen and a CO_2-rich recycled flue gas resulting in a product flue gas containing mainly CO_2 and water. Chemical looping combustion is considered by some to be a special case of oxyfuel combustion. In chemical looping combustion metal oxides are used to provide oxygen. Pre-combustion capture involves reacting a fuel with oxygen or air and/or steam to give mainly a 'synthesis gas (syngas)' or 'fuel gas' composed of carbon monoxide and hydrogen. The carbon monoxide is reacted with steam in a catalytic reactor, called a shift converter, to produce CO_2 and more hydrogen. CO_2 is then separated, usually by a physical or chemical absorption process, resulting in a hydrogen-rich fuel which can be used in many applications, such as boilers, furnaces, gas turbines, engines and fuel cells. Figure 1 shows the three systems in schematic form.

All these systems have been reviewed in IEA Clean Coal Centre reports:

 . *Post-combustion carbon capture from coal fired plants – solvent scrubbing* (Davidson, 2007);
 . *Post-combustion carbon capture – solid sorbents and membranes* (Davidson, 2009);
 . *Oxyfuel combustion of pulverised coal* (Davidson and Santos, 2010);
 . *Chemical looping combustion of coal* (Henderson, 2010);
 . *Pre-combustion capture of CO2 in IGCC plants* (Davidson, 2011).
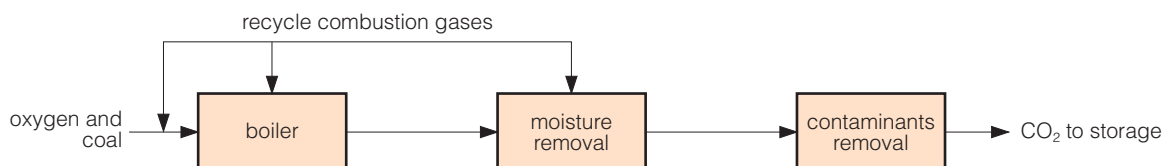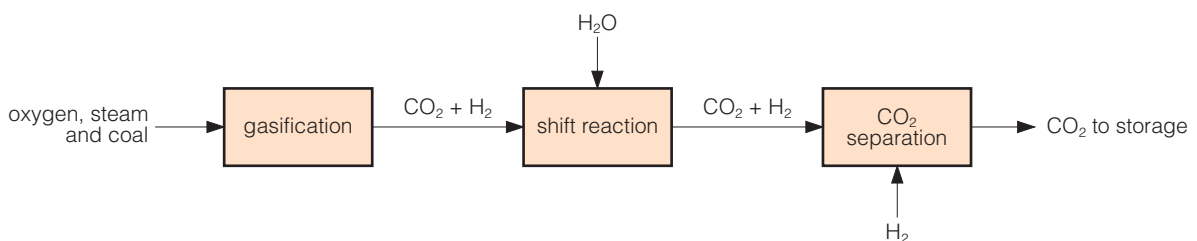

Figure 1 CO_2 capture systems

However, Favre and others (2009), comparing post-combustion capture with oxyfuel combustion noted that: *Surprisingly, the two options . . . have always been seen as distinct and, somehow, competing*. Recently, there have been signs that this is no longer the case. Some researchers have realised that it may be possible to pick and choose among the elements of the main CO_2 capture systems and develop hybrid systems which are possibly cheaper and more energy efficient. Most hybrid systems are at a very early stage of development compared with the conventional methods with much of the research aimed at evaluation or modelling. This report will look at these proposed systems.

2 Post-combustion capture with oxygen enriched combustion

Favre and others (2009) considered a combination of enriched oxygen combustion with post-combustion capture. They evaluated a tentative capture framework which combined an oxygen enrichment step before combustion and a CO_2 capture step from flue gas through a simulation study of a natural gas power plant. The performances of a cryogenic oxygen production process were used for the upstream part, while a membrane separation process based on CO_2 selective materials has been investigated for CO_2 capture. It was found that the hybrid process could lead to a 35% decrease in the energy requirement (expressed in GJ/t of recovered CO_2) compared with oxycombustion, providing that the optimal oxygen purity is used (typically 40–60%) in combination with a membrane module with a CO_2/N_2 selectivity of 50 or more.

The use of a membrane module for post-combustion capture becomes possible because the oxygen enrichment produces a higher content of CO_2 in the resulting flue gas. In the report on the use of membranes for post-combustion capture (Davidson, 2009) it was noted that Bounaceur and others (2006a,b) had concluded that, for membranes to compete with solvent absorption in terms of energy requirement, the CO_2 content of the feed gas must exceed 20%.

Although Favre and others' (2009) study was based on a natural gas power station, a study by Doukelis and others (2009) considered the cases of a 330 MWe Greek lignite plant and a typical 600 MWe hard coal plant. Their proposed concept was called ECO-Scrub and was based on partial oxyfuel combustion in the furnace followed by post-combustion solvent scrubbing. A schematic diagram is shown in Figure 2.

The O_2 volume concentration in the total air was selected to be equal to 30% and in the secondary air 32.28%, so that all pipes are constructed by common materials without any effect on cost. Also, this concentration demands minor modification in the boiler and a limited flue gas recirculation. The CO_2 volume concentration in net and dry flue gas (at inlet of scrubber) was just over 23% for both reference plants. The CO_2 absorber was a 30 wt% solution of monoethanolamine (MEA).
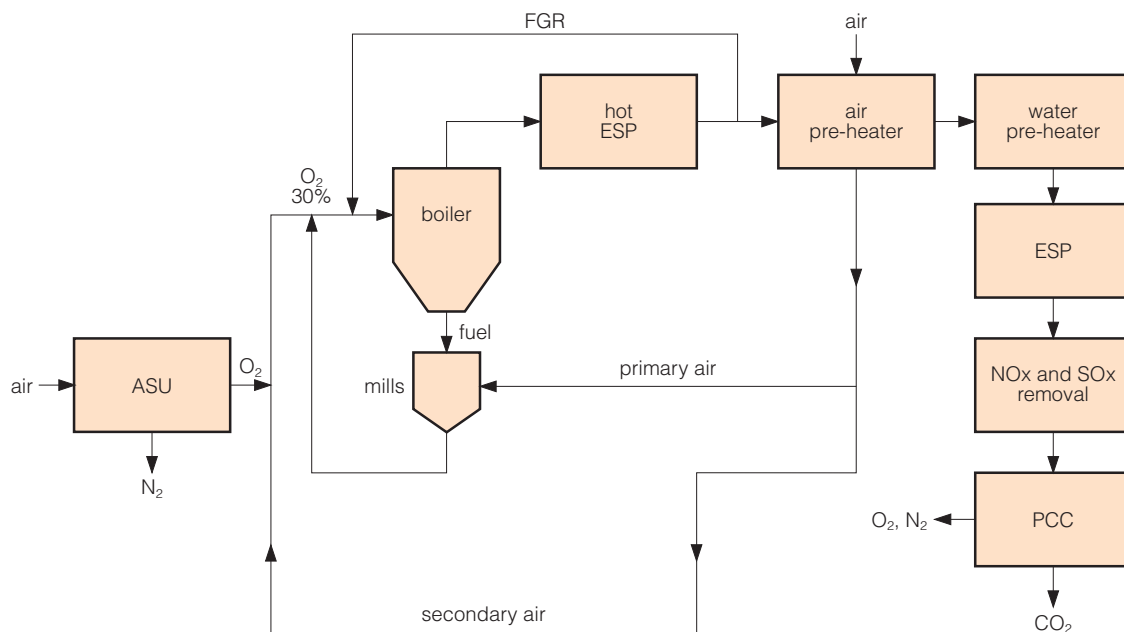

Figure 2   Enhanced O_2 coal power plant with post-combustion CO_2 capture (Doukelis and others, 2009)

Table 1 Main results-comparison for 600 MWe hard coal plant (Doukelis and others, 2009)				
	Reference case	Retrofit case (post-combustion)	Retrofit case (oxyfuel)	Retrofit case (ECO-Scrub)
Gross electric power, MWe	613.86	508.31	632.7	557.26
Gross electrical efficiency, %	47.22	39.10	48.67	42.87
Net electric power, MWe	588	426.13	468.34	455.01
Net electrical efficiency, %	45.23	32.78	36.03	34.97
CO_2 compressors electric consumption, MWe		38.9	38.9	38.9
ASU electric consumption, MWe			81.2	37.4
Reboiler duty, MWth		461		329.3
O_2 in total air, vol%	21	21	95	30

Simulations were performed using the IPSEpro program for both power plants for the following cases:
1 existing power plant (reference case);
2 power plant with oxyfuel combustion (as retrofit case);
3 power plant with post-combustion CO_2 capture (as retrofit case);
4 power plant with incorporation of ECO-Scrub technology (as retrofit case);.

The minimum capture level of CO_2 was set at 95 vol% for the capture cases. The main results for the 600 MWe plant are shown in Table 1.

The main conclusions reached were that, compared with both pure oxyfuel and post-combustion CO_2 capture technologies, the ECO-Scrub technology:
. the total electricity generation cost (per net electricity) is lower;
. the simultaneous use of an air separation unit (ASU) and post-combustion scrubber has a lower energy penalty.

Compared with pure post-combustion CO_2 capture technology:
. it has higher gross and net electric efficiency;
. it needs less heat energy for the reboiler duty;
. it needs less amine mass in the scrubbing plant for CO_2 capture.

Compared with pure oxyfuel combustion the ECO-Scrub technology needs less energy for the ASU. On the other hand, it has lower gross and net electric production. Even so, it was still seen as more attractive as a retrofitting option because the oxyfuel technology:
. requires many and serious modifications at the boiler island;
. has higher fixed capital and operating costs;
. has a higher electricity generation cost.

Dynamic modelling by Lawal and others (2010) showed (what must have been the obvious result) that less solvent is needed to capture CO_2 because its concentration in the flue gas stream is significantly higher. As the solvent circulation rate reduces, the heat duty requirement for capture also reduces. Later, Lawal and others (2011) extended their studies to encompass O_2 concentrations in the primary and secondary air ranging from 21 vol% to 50 vol%. The gPROMS advanced process modelling environment was used to develop dynamic models. The models showed that higher CO_2 partial pressures in the flue gas led to reduced energy requirements for capture. However, the absorber operating temperatures were also increased with increasing CO_2 concentration. This is because more heat of reaction is released and there is less quantity of gas to exchange heat with. The performance of the system could possibly be improved if absorber temperatures were minimised.

3 Regenerable sorbents with oxyfuel combustion

The use of natural, usually limestone, regenerable sorbents for post-combustion capture has been addressed in an IEA CCC report on *solid sorbents and membranes* (Davidson, 2009). However, in that report the emphasis was mainly on the behaviour and properties of the regenerable sorbents including their deactivation and ways of improving their performance in regeneration and recycling. However, the use of regenerable sorbents can also be viewed as a form of hybrid carbon capture in that oxyfuel combustion can be used to provide the heat required to operate the limestone calciner at temperatures above 900°C. In this chapter the emphasis will be on regenerable sorbent capture (calcium looping) combined with oxyfuel combustion.

Lu and others (2007, 2008a,b) have reported results from 75 kWth pilot-scale atmospheric dual fluidised bed combustion system for in situ CO_2 capture which was constructed by CANMET in Canada. The system consists of two fluidised bed reactors: a sorbent calciner/regenerator, which is a circulating fluidised bed combustor upgraded for operation with oxyfuel firing using flue gas recycle, and a combustor/carbonator, which is divided into two stages and designed for the separation of combustion/sulphation and carbonation. A high CO_2 capture efficiency (>90%) was achieved for the first several cycles, which decreased to a still acceptable level (~75%) even after more than 25 cycles. Lu and others (2008b) have pointed out that, initially, external electric heaters were used with the calciner but that this does not represent a practical situation. Hence, the use of oxyfuel combustion to provide the heat source. In the tests the O_2 concentration was ~40–50 vol% with the flue gas recycle making up the remaining 50–60 vol%. A CO_2 concentration from the calciner off-gas of ~85 vol% was achieved. Improving the unit design to minimise air ingress was expected to produce higher levels.

Abanades and others (2007; *also* Romeo and others, 2006) considered the cost structure of a system using regenerable limestone sorbents in which the exhausted calcines have some downstream value as a feedstock for the cement industry. They presented the basic economics of a complete system including three key cost components:

. a full combustion power plant;
. a second power plant working as an oxyfired circulating fluidised bed calciner (CFBC);
. a fluidised bed carbonator interconnected with the calciner and capturing CO_2 from the combustion power plant.

The key cost data for the two major first components are well established in the open literature. It was shown that there is scope for a breakthrough in capture cost to around 15 $/t of CO_2 avoided with this system. This is mainly because the capture system is generating additional power (from the additional coal fed to the calciner) and because the avoided CO_2 comes from the capture of the CO_2 generated by the coal fed to the calciner and the CO_2 captured (as $CaCO_3$) from the flue gases of the existing power plant, that is also released in the calciner. Put simply, the oxyfired CFBC is not only avoiding the CO_2 from its own coal combustion feed, but all the CO_2 coming from the flue gases of the neighbouring power plant. The oxyfired plant captures about twice the CO_2 than it generates from the combustion of its own coal feed. An outline of the system is shown in Figure 3 (Abanades, 2011).

As indicated in Figure 3, the CO_2 captured from the flue gases as $CaCO_3$ and the CO_2 produced by the oxyfired combustion of coal in the calciner are recovered in concentrated form from the calciner gas. A considerable fraction (40–55%) of the total energy entering the system is used in the calciner. Most of this energy leaves the system in mass streams at high temperature (at >900°C) or is recovered as carbonation heat in the carbonator (at around 650°C). Thus, the large energy input into the calciner comes out of the system as high quality heat that can be used in a highly efficient steam cycle. Romeo and others (2008) have pointed out that post-combustion Ca looping is the only capture system that introduces repowering to the existing power plant because the calciner is indeed very similar to a new
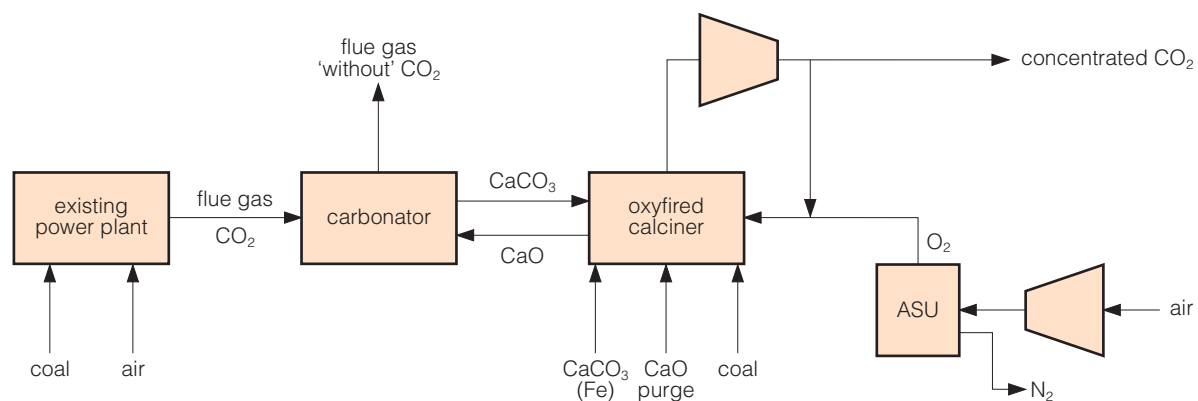
Figure 3   Post-combustion Ca looping system with an oxyfired calciner (Abanades, 2011)

oxyfired fluidised bed power plant. Further, under these conditions, the capture system is able to generate additional power at 26.7% efficiency (LHV) after accounting for all the penalties in the overall system, without disturbing the steam cycle of the reference plant that retains its 44.9% efficiency. A preliminary cost study of the overall system produced a capture cost around 16 €/tCO$_2$ avoided and an incremental cost of electricity of just over 1 €/MWh.

Romano (2009) compared the thermal efficiency of a coal-fired power plant with calcium oxide carbonation for post-combustion CO$_2$ capture, regenerated in a fluidised bed calciner via oxyfuel combustion of coal with full oxyfuel combustion and amine based plants. He calculated a net LHV efficiency of 37.4% for the selected reference case, with 97% of the CO$_2$ captured, compared with 36.3% for full oxyfuel combustion and 32.6% for the amine based plant. However, it was conceded that plant complexity is higher than the competitive technologies.

Table 2	Main inputs to Ca looping pilot plant (Sánchez-Biezma and others, 2011b)
Flue gas flow to carbonator, kg/h	680–2400
Maximum coal flow to calciner, kg/h	325
Maximum fresh limestone flow, kg/h	300
Oxygen flow to calciner, kg/h	300–600
CO$_2$ flow to calciner, kg/h	700–2250
Air flow to calciner, kg/h	600–2500

A 1.7 MWth pilot test facility built at La Pereda power plant (Spain) to test the concept is described by Sánchez-Biezma and others (2011a,b). The pilot plant is designed to capture 70–95% of the CO$_2$ contained in the flue gas from a 1/150 side stream emitted by the existing 50 MWe CFB power plant. The experimental work plan includes the operation of the CFBC calciner in oxyfuel combustion mode under different O$_2$/CO$_2$ ratios, with O$_2$ and CO$_2$ supplied from liquefied tanks. The main inputs to the pilot plant are listed in Table 2 (Sánchez-Biezma and others, 2011b).

4   Post-combustion capture in IGCC plants

Higman (2007) has pointed out that it is worthwhile for the IGCC community to monitor improvements in post-combustion CO_2 capture, because anything in this area that applies to a PC unit could also be used on an IGCC. It should be noted that, after the gas turbine combustor, about 9% carbon dioxide exits in the flue gas and partial pressure of the carbon dioxide is low. However, Kunze and Spliethoff (2011, 2012; Kunze and others, 2011) have suggested that a post-combustion approach might produce a significant increase in net efficiency compared with a conventional IGCC plant.

In the plant design shown in Figure 4 neither a CO conversion nor a CO_2 capture unit is part of the gas treatment section. The physical enthalpy of the hot raw gas is used in the heat recovery steam generator (HRSG) to produce supercritical steam. Afterwards the particles are removed from the approximately 230°C cold gas. The gas is washed to remove water soluble species such as ammonia and chlorine containing components. The sulphur is removed by an MDEA absorption process. Since the washing process is not very efficient in COS removal an additional COS/HCN hydrolysis is required up-stream. The recovered H_2S is converted to elemental sulphur in an air based Claus plant. Finally, the major part of the carbon containing fuel gas is burnt in the gas turbine. A limestone based carbonate looping process is used for CO_2 capture.

The performance of this proposed plant was analysed and compared with a conventional IGCC plant with pre-combustion capture for similar operating parameters (Kunze and Spliethoff, 2011). For the simulations the commercial simulation software Aspen Plus™ was used for the gas production as well as the gas processing part and Ebsilon Professional for the combined cycle section. In the simulations the efficiency for the proposed concept was found to be substantially higher than the base case concept. For a plant combining IGCC with carbonate looping (IGCC-CL), the simulation showed an efficiency of 51.6% (gross) and 40.6% (net). This represents a significant improvement of 3.9 % points in gross efficiency compared with the base case. However, due to a substantial increase of the utility demand, especially for the nitrogen compressor, the resulting plant net efficiency is only 1.22 % points higher than in the base case. This was described as a rather low improvement considering the uncertainties of the simulation assumptions and the expected initial difficulties when combining new technologies.
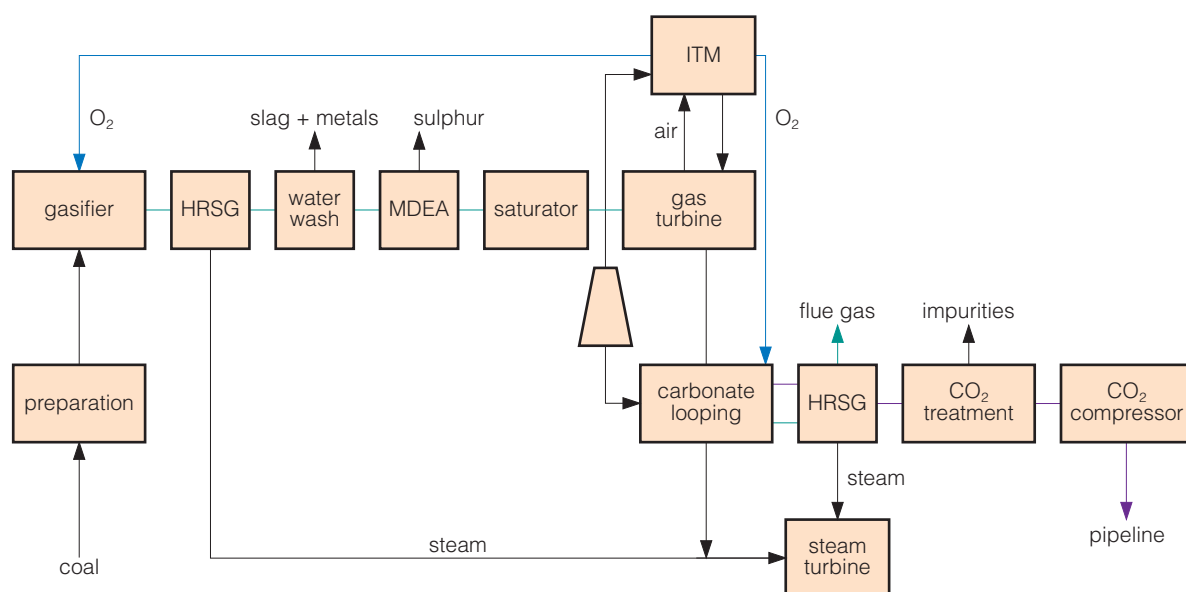

Figure 4   Advanced IGCC process with Ca looping CO_2 capture (Kunze and Spliethoff, 2011)

Kunze and Spliethoff (2012) produced revised figures which were based on the conventional ASU being replaced by a fully integrated oxygen transfer membrane process (OTM). This substitution reduced utility demand by 37%, resulting in a net efficiency gain of 2.47%. Hence the combination of OTM and carbonate looping leads to synergy effects, especially due to the high oxygen demand, direct utilisation of hot low-pressure oxygen in the oxycombustor and recycling of the hot air stream to the combustion chamber. In summary, the proposed IGCC-CL concept achieved a net efficiency of 45.87% (LHV). The combination of high efficiency and a CO_2 recovery of 97.7% results in moderate specific CO_2 emissions in the range of 17.1 g/kWh. It was concluded that a favourable efficiency potential (45.87%) can only be achieved with an integrated OTM process. The high dependence on both the carbonate looping and the OTM assumptions implies a higher uncertainty of the simulation results and a possible future realisation. Furthermore, the high level of integration might lead to reduced flexibility and reduced availability of the plant.

Cormos (2011; *also* Cormos and others, 2011) performed modelling and simulation studies comparing carbon capture options for 400–500 MW (net) IGCC plants using coal and biomass (sawdust). These indicated that post-combustion capture using MDEA is marginally less efficient by about 0.5% points in terms of net electrical efficiency compared with pre-combustion capture using the same solvent. Compared with pre-combustion capture using Selexol® process, post-combustion capture using MDEA is less efficient by about 1% point. This is due to the heat needed for solvent regeneration (much more compared with physical solvents) and the difference in term of carbon dioxide partial pressure in the gases between post-combustion and pre-combustion situations.

5   Gasification with oxyfuel

A process named *integrated gasification steam cycle* (IGSC) has been described by Griffiths (2008, 2010). The concept of IGSC is through the gasification of coal in a quench gasifier, followed by combustion of the resulting syngas, with oxygen and water, in a modified gas turbine fitted with a novel form of oxy-burner, the CES burner, derived from rocket technology and developed by Clean Energy Systems. These burners use recycled water rather than recycled CO_2 to moderate the temperature. The burners are mounted annularly in a commercial gas turbine (the 'fired expander') to generate power and the hot exhaust gases are passed through a heat recovery steam generator (HRSG) then used to raise steam to drive a conventional steam turbine. A flowsheet is shown in Figure 5.
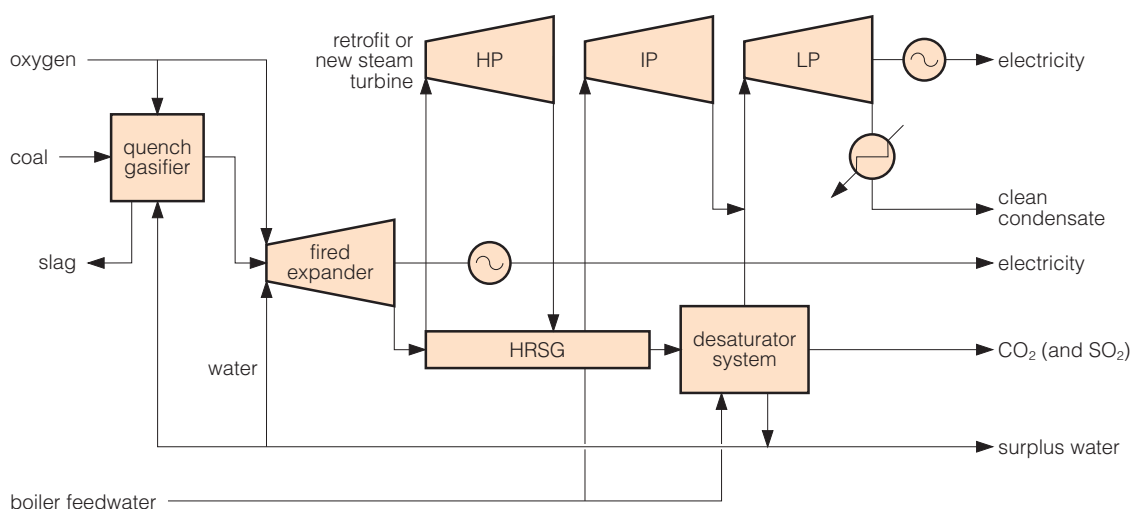

Figure 5   Integrated gasification steam cycle (Griffiths, 2008)

Downstream of the HRSG, the exhaust gases, which consist of steam mixed with CO_2, are directly quenched with circulating cold water to condense all the steam, leaving the CO_2 to be collected and compressed. The plant has no sulphur dioxide control unit. SO_2 is captured along with the CO_2 with the favoured option of the Air Products process. The CO_2 is compressed together with some oxygen and water resulting in the conversion of SO_2 to sulphuric acid which can be removed between compression stages.

The IGSC is claimed to be very suitable as a retrofit to existing coal-fired power stations resulting in 100% CO_2 capture and an increase in electricity output of about 60%.

Air Products has also developed a process combining gasification with oxycombustion which is claimed to reduce the cost of CO_2 capture by over 25% (Hufton and others, 2011). The system combines a sour PSA unit for capturing CO_2 and H_2S, with a low CV sour oxycombustion unit applied to the tail gas to extract available heat energy from the combustible components. This then feeds into a proprietary compression system that is simultaneously able to purify and remove undesirable trace components from the CO_2 rich product gas. A flowsheet is shown in Figure 6.

Unlike the IGSC system, the Air Products system still uses a shift reactor to convert the syngas into mainly H_2 and CO_2, the major benefit of the oxyfuel combustor is to convert the H_2S in the sour gas into SO_2 which can then be captured in the CO_2 purification/compression stage. The other major benefits claimed for the technology are:
  . 100% CO_2 capture possible;
  . major cost savings compared with conventional physical solvent absorption process;
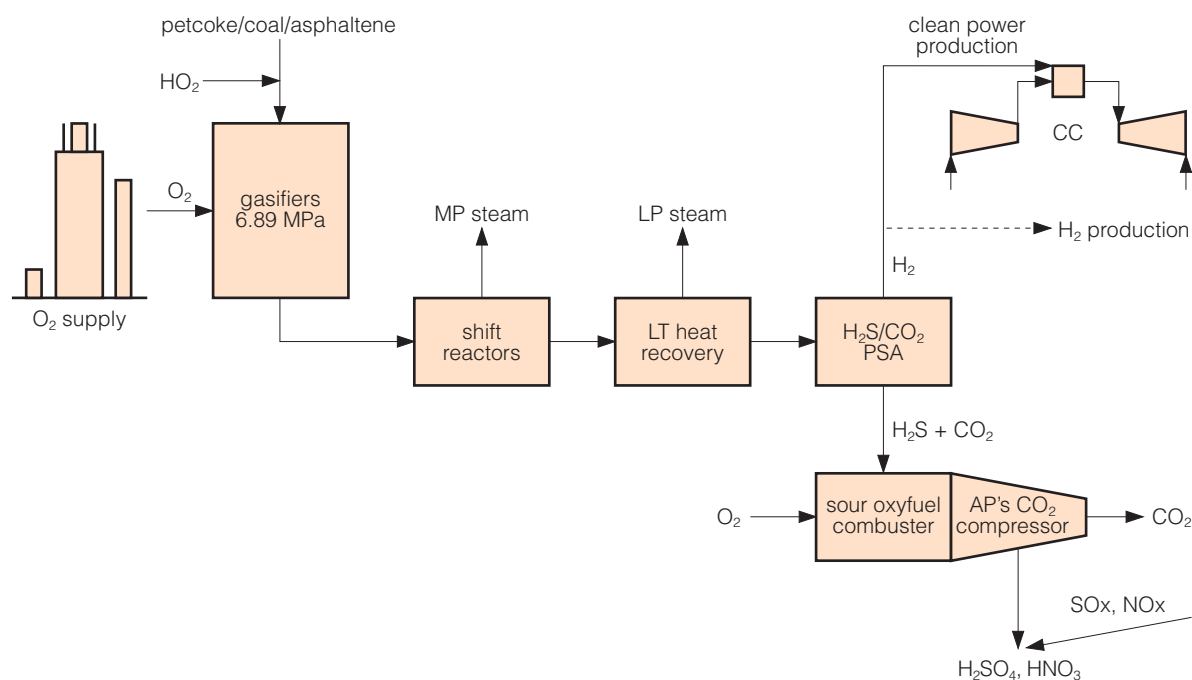 . amenable for polygeneration.

Figure 6   Sour oxycombustion CO_2 capture for gasification (Hufton and others, 2011)
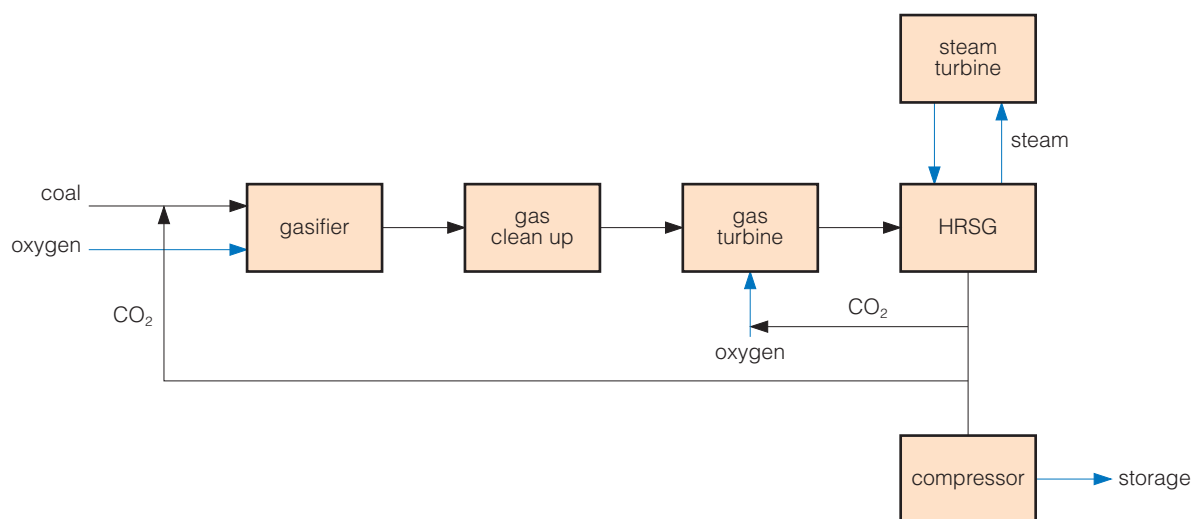

Figure 7   Oxyfuel IGCC (Oki and others, 2011)

In another oxyfuel variant, CRIEPI, Japan, have developed an oxyfuel IGCC system in which the coal is gasified in a mixture of O_2 and recycled CO_2 flue gas as in an oxyfuel combustion process (Oki and others, 2011; Inumaru and others, 2011). Therefore, compared with a conventional pre-combustion system, a shift reactor and CO_2 capture unit are not required. A schematic of the process is shown in Figure 7. The absence of a shift reactor and CO_2 capture unit results in the thermal efficiency of this system remaining above 40% even after capturing CO_2.

CO_2 can also act as gasification agent, therefore an increase of CO_2 concentration in the gasifier is expected to enhance the gasification efficiency of gasifier, comparing with the gasification efficiency of oxygen blown gasification. CRIEPI have estimated potential improvement in cold gas efficiency of 2% and a drastic reduction in the formation of char attributable to the gasification reactions enhanced by higher concentrations of CO_2. In planned further studies, CRIEPI's 3 t/d gasifier will be used in conjunction with an online sampling scheme. This gasifier is essentially a two staged air-blown unit, but it can vary O_2 concentration between 0% to 30%. Recent modifications in the form of a CO_2 gas supply system will facilitate evaluations of the effect of CO_2 gas on coal gasification performance.

A potential drawback of a high CO_2 concentration syngas is carbon deposition, because deposition in the desulphurisation matrix may deteriorate the catalyst. To clarify the risks of carbon deposition in the hot gas clean-up system and develop a method to prevent the deterioration of the catalyst, further studies have been carried out. In general, carbon deposition in high CO concentration gas was mainly affected by two reactions, but in this system, the Boudouard reaction is the most important. The data obtained was processed using an index calculated from the partial pressures of CO and CO_2. Experimental data have confirmed that this index plays quite an important role. If the index is high enough, carbon does not deposit. So, to prevent carbon deposition, the index can be adjusted in the hot gas clean-up system (Inumaru and others, 2011).

An IGCC concept which applies hot gas clean-up and combustion of the unconverted fuel gas using pure oxygen was assessed and simulated by Kunze and Spliethoff (2012). The oxygen is supplied by an integrated oxygen transfer membrane. The combination of IGCC and the oxyfuel process reached a net efficiency of 45.74% (LHV). Despite the high efficiency, the specific CO_2 emissions are comparably high (20.4 g/kWh) due to the lower CO_2 capture rate of 96% caused by the slip of CO_2 during air pre-heating in the OTM process. The specific carbon emissions of an oxy-concept incorporating a cryogenic ASU were found to be much lower (7.1 g/kWh) despite the lower efficiency. It was concluded that the concept implies considerable modifications in the combined cycle section as well as entirely new equipment. Due to the combustion in pure oxygen and different working fluid, a new gas turbine and condenser are required. It seems highly doubtful that the high monetary and constructional effort will be dedicated in the future despite the high thermodynamic potential of the concept.

6 Gasification with chemical looping

Chemical looping combustion (CLC) is an indirect form of combustion in which an oxygen-containing solid material, typically a metal oxide, supplies the oxygen to a fuel, and the spent oxygen 'carrier' is separately regenerated by high temperature reaction in an air stream. As there is no direct contact between air and fuel, CO_2 recovery up to very high levels is simplified. The chemical looping combustion of coal and syngas has recently been reviewed by Henderson (2010). Chemical looping combustion is normally used to generate heat. However, chemical looping can also be integrated with gasification as a means of separating CO_2 and producing hydrogen. As Li and Fan (2008) have pointed out, compared with the CLC processes, the syngas chemical looping (SCL) process has the flexibility to co-produce hydrogen and electricity.

A process called the syngas redox (SGR) process to produce hydrogen from coal derived syngas was described by Gupta and others (2007; *also* Velazquez-Vargas and others, 2006). The process involved reduction of a metal oxide to metallic form with syngas and subsequent regeneration with steam to generate hydrogen in a cyclic operation. Metal oxides of Ni, Cu, Cd, Co, Mn, Sn and Fe were evaluated for this process based upon thermodynamic equilibrium limitations. A simplified schematic is shown in Figure 8. In the reduction part of the process, coal derived syngas is used to reduce the metal oxide (MO) to the metal form (M):

$$MO + CO/H_2 \leftrightarrow M + CO_2/H_2O$$

In the oxidation side, the metallic form is oxidised back to the metal oxide which can be used again in another redox cycle. The oxidation is carried out using steam which leads to the formation of hydrogen.

$$M + H_2O \leftrightarrow MO + H_2$$
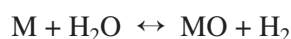
Detailed process simulation showed that the SGR process is capable of converting 74% of the coal energy into hydrogen energy on a higher heating value (HHV) basis, which is higher than the water-gas shift (WGS) process (64%), while delivering a pure CO_2 stream without the need for costly separation technology.
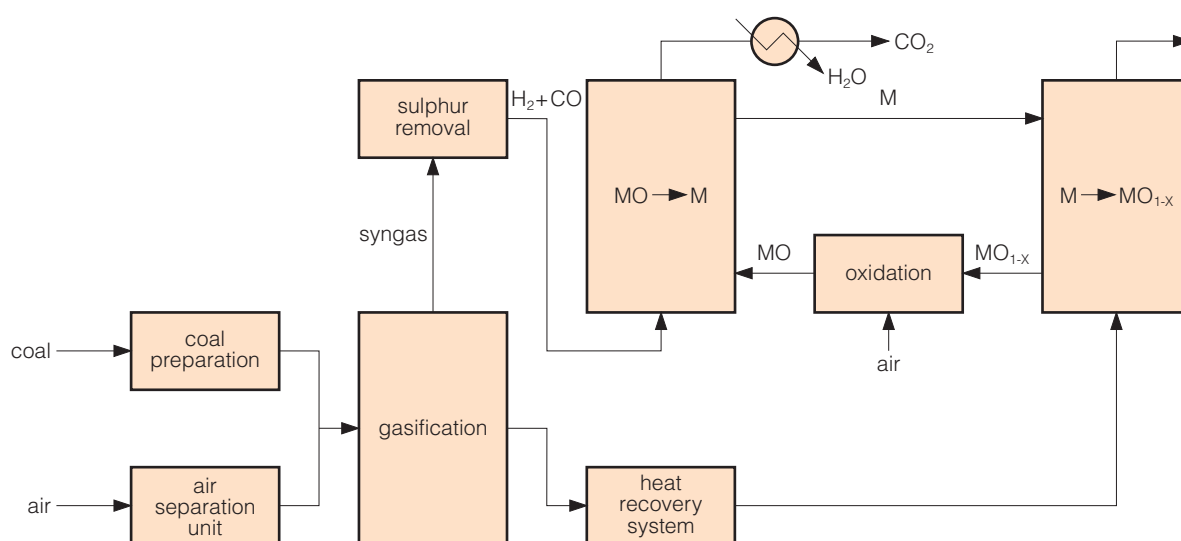

Figure 8 Syngas redox process for hydrogen production from coal (Velazquez-Vargas and others, 2006)
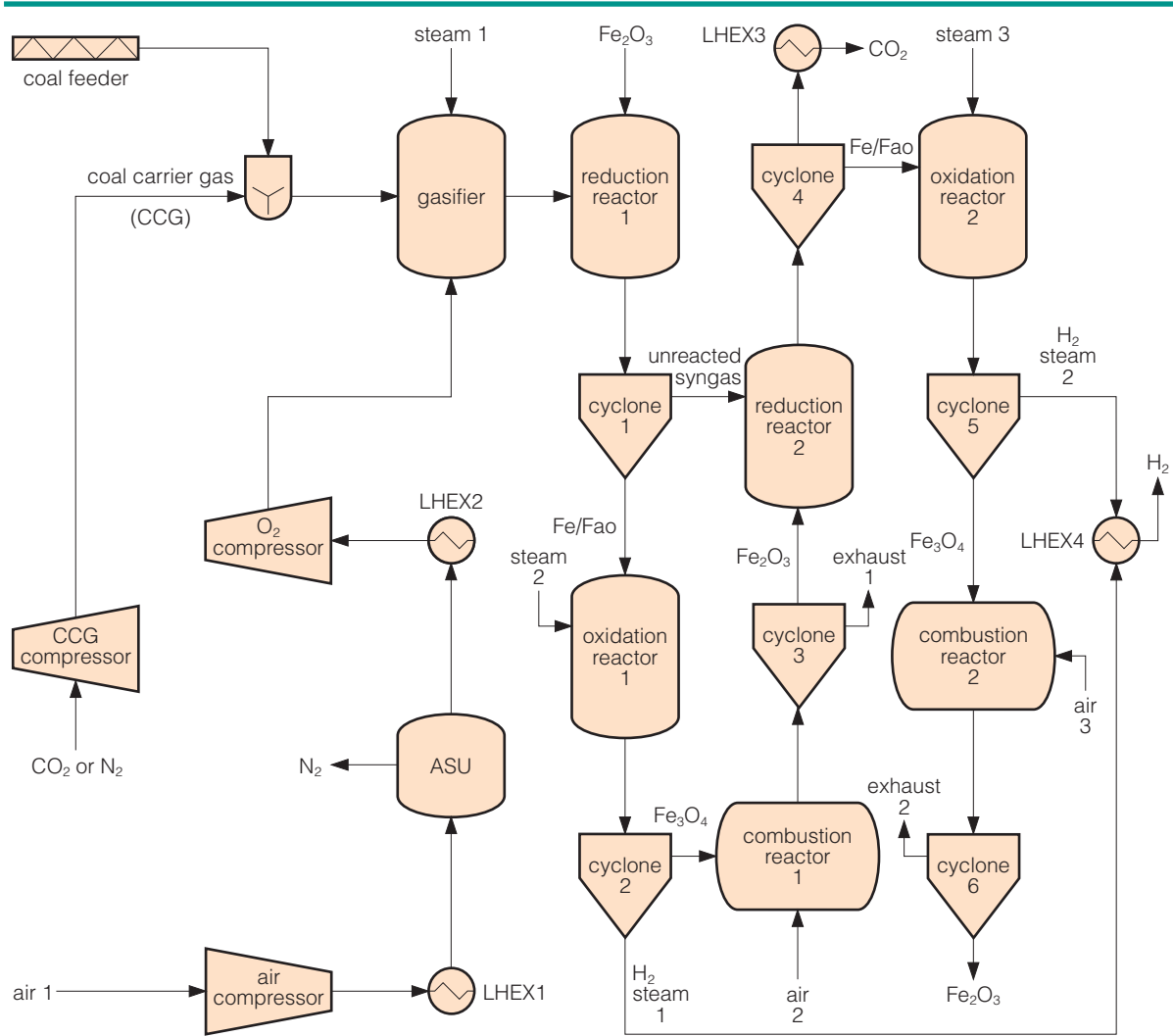
Figure 9   Syngas chemical looping combustion system (Gnanapragasam and others, 2009)

From a study of oxygen carrier particles, it was found that Fe_2O_3 provided the best conversion of syngas to combustion products CO_2 and H_2O along with a high conversion of steam to hydrogen (Li and others, 2009). Adding supports to the iron oxide drastically increased the reactivity and recyclability of the oxygen carrier. TGA experiments showed that the iron oxide composite particle can maintain recyclability for more than 100 cycles. During the reduction stage, more than 99.75% of syngas was converted into steam and CO_2. Meanwhile, the oxygen carrier particle was reduced by nearly 95% with minimal carbon deposition. During the steam oxidation stage, an average hydrogen purity of 99.8% (dry, N_2 free basis) was obtained.

Chemical looping as a replacement for the WGS reaction as a means of producing CO_2 and H_2 subsequent to gasification has also been studied by Gnanapragasam and others (2009). A schematic of their system is shown in Figure 9.

The syngas produced from the gasifier contains mostly CO, H_2, CO_2 and CH_4 and it reduces the metal oxide (Fe_2O_3) to the constituent metal (Fe and FeO). The advantage of using iron oxide (Fe_2O_3) as the oxygen carrier is that it does not involve catalytically dependent reactions. The gaseous products are CO_2 and steam. The steam is condensed to obtain sequestration-ready CO_2. The subsequent oxidation (or hydrogen) reactor operates at 30 atm and 500–700°C to oxidise the metal produced in the reduction reactor using steam. The products are 99% pure hydrogen and magnetite (Fe_3O_4). Hydrogen production using chemical looping combustion of the syngas is indirect with the use of iron oxide. The actual hydrogen in the syngas is converted to water in the first reduction reactor. Gnanapragasam
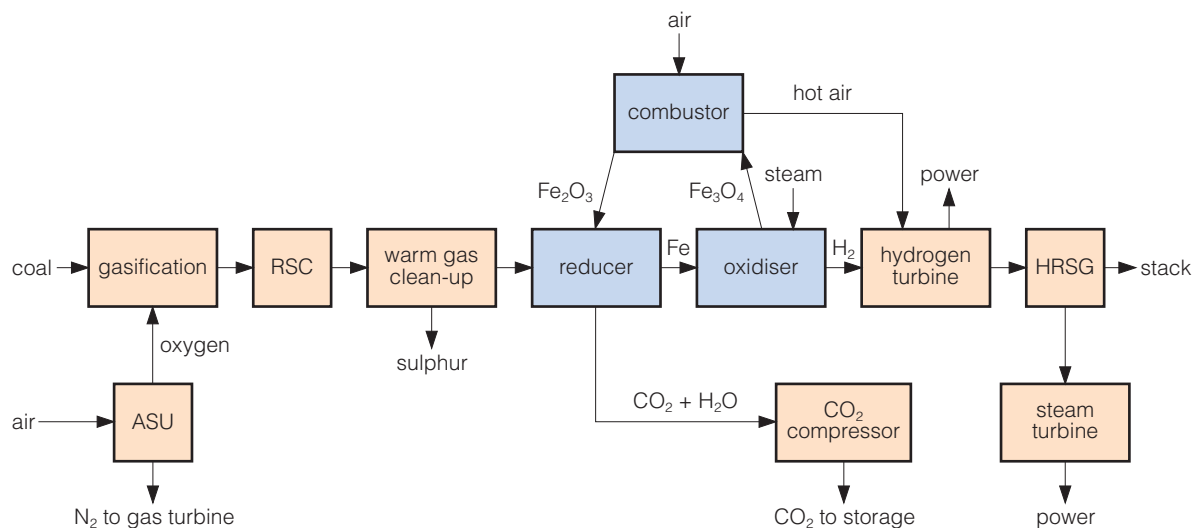
Figure 10 Syngas chemical looping for CO$_2$ separation (Plunkett and others, 2009b)

and others (2009) also discussed the use of coal direct chemical looping as a substitute for the gasification process.

Plunkett and others (2009a,b) used Aspen Plus™ to compare conventional CO$_2$ capture in an IGCC plant with alternate methods of pre-combustion capture. One method examined was warm gas clean-up with SCL for CO$_2$ separation. In this process, CO reduction of Fe$_2$O$_3$ separates the CO$_2$ stream at high pressure (~5 MPa) then oxidation of Fe produces H$_2$ fuel for the turbine. Further oxidation of Fe$_3$O$_4$ supplies hot air to the turbine. A schematic is shown in Figure 10.

The modelling studies indicated that advanced technologies such as syngas chemical looping paired with warm gas clean-up have the potential to significantly reduce the performance and cost impact of CO$_2$ separation, having the potential to reduce COE by 10–15 % compared with conventional physical absorption. The net plant efficiency on an HHV basis increased from 32.5% for the conventional system to 36.4% using SCL. However, it was noted that SCL is likely to encounter engineering challenges with respect to hot solids transfer, heat integration, and kinetics during its development towards commercialisation. The analysis of SCL technology assumed:
1   complete reaction of syngas with iron oxide to produce iron, CO$_2$, and water;
2   smooth operation and integration between the reducer and oxidiser reactors.

Similar calculations for a system using hydrogen membranes produced results very close to those found for the SCL system. However, the net plant power of the SCL system at 605 MW was remarkably close to that of the reference IGCC plant operating without capture.

The techno-economic characteristics of four different pre-combustion capture technologies, which are built upon a conventional IGCC reference case, were studied by Rezvani and others (2009) using the chemical process simulation package 'ECLIPSE'. The technology options considered were: physical absorption, water gas shift reactor membranes and two CLC cycles, which employ single and double stage reactors. The latter system was devised to achieve a more balanced distribution of temperatures across the reactors and to counteract hot spots which lead to the agglomeration and the sintering of oxygen carriers. The oxygen carrier selected for the CLC process was a nickel based material stabilised with 40% alumina (NiO/Al$_2$O$_3$). Air was used in the oxidation reactor rather than steam, thus this system is not able to co-produce hydrogen. The compressed air and the recycled oxygen carrier enter the air reactor (AR) with a residence time between 4 and 11 s. In the reactor under an exothermic reaction, nickel oxidises to nickel oxide before it travels via a cyclone into the fuel reactor (FR). Here, two simultaneous processes take place: the reduction process of the oxygen carrier and the oxidation of the syngas. The residence time of the oxygen carrier in the fuel reactor is up to 60 s. The
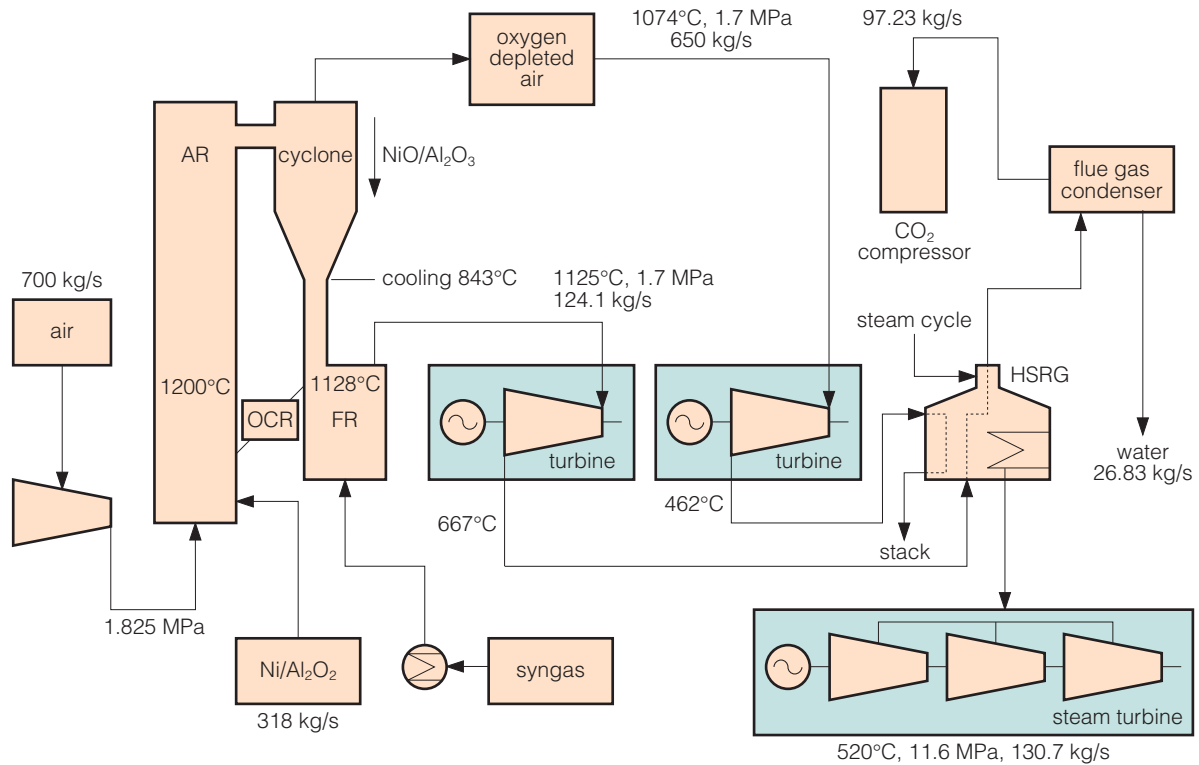
Figure 11 IGCC system with integrated chemical looping combustion (Rezvani and others, 2009)

oxygen depleted air leaves the cyclone at a temperature of above 1000°C and runs through an expander for power generation. The gas continues its journey through a number of heat exchangers to raise steam before it leaves the stack. In parallel, the CO_2-rich gas from the fuel reactor runs through the gas turbine, through the heat exchangers for steam generation and through the flue gas condenser, before it enters the CO_2 compression train. The generated steam is utilised in steam turbines to generate electricity. A schematic is shown in Figure 11.

Despite the lowest efficiency loss among the studied systems, the economic performance of the double stage CLC was outperformed by systems employing physical absorption and water gas shift reactor membranes. As a result of the high plant efficiency and the relatively low capital cost, the system with WGS membrane reactors outperforms the other cases in terms of CO_2 avoidance costs. Due to high capital investments and operating costs, the CO_2 avoidance costs for CLC systems, in particular the double stage CLC option, were found to be exceptionally high.

Cormos (2010) evaluated a chemical looping system, using iron oxides as an oxygen carrier, in conjunction with co-gasification of coal and biomass (sawdust) with carbon capture and storage (CCS). Steam was used in the oxidation reactor to regenerate the iron oxide and to produce hydrogen. Hydrogen and electricity co-production schemes were modelled and simulated using process flow modelling software (ChemCAD). Based on the modelling, it was concluded that chemical looping systems used for carbon capture imply lower energy penalties compared with more classical carbon capture technologies like gas-liquid absorption.

Cormos (2011; *also* Cormos and others, 2011) assessed and compared various methods for carbon dioxide capture applicable to power generation based on an IGCC scheme. The evaluated carbon capture options were: post-combustion capture applied to the flue gases coming from the gas turbine using chemical solvents (for example, methyldiethanolamine – MDEA) and pre-combustion capture using either gas-liquid absorption (chemical and physical solvents) or an iron based chemical looping system applied to the syngas. The case studies investigated produce about 400–500 MW net electricity

with more than 90% carbon capture rate considering all carbon feedstock (including biomass). The modelling revealed that the IGCC scheme with CCS based on the chemical looping system is significantly more efficient than the one based on Selexol® pre-combustion capture by about 1.8% points in terms of net electrical efficiency. It was pointed out that the superior efficiency of the iron-based chemical looping system in comparison with gas-liquid absorption (either physical or chemical absorption) is even more significant considering that there is an almost totally decarbonisation of the fuel used, 99.51% carbon capture rate as opposed to 90.79% using Selexol®.
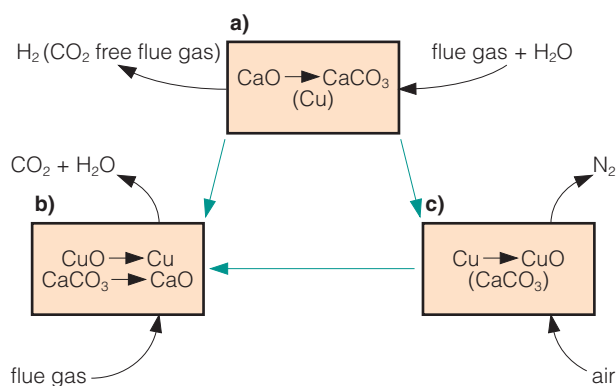
Figure 12 Cu/Ca three step chemical loop
(Abanades, 2011)

The status of calcium looping processes for H_2 production is briefly discussed by Abanades (2011; *see also* Davidson, 2011). In this process, CO_2 is removed in situ by CaO, so that the WGS reaction occurs simultaneously with CO_2 capture. However, the main hurdle for successful scaling up of these technologies for CCS may not be in the H_2 generation step, but in the $CaCO_3$ regeneration step within a CO_2-rich atmosphere. If the reactions are carried out in a fluidised bed at high pressure, the calcination in oxyfuel conditions is very challenging because the equilibrium dictates operating temperature higher than 1000°C (material issues and rapid sorbent deactivation over 950°C do not favour these conditions). If the reactions are carried out in fixed bed systems, it is also very challenging to supply the heat for calcination to the fixed bed of solids. Abanades (2011) has proposed a novel process to overcome these difficulties that is represented in Figure 12.

Although developed for reforming of and hydrogen production from natural gas, it was noted that the fuel gas can be derived from gasification. Step A is a conventional sorption enhanced reaction in the
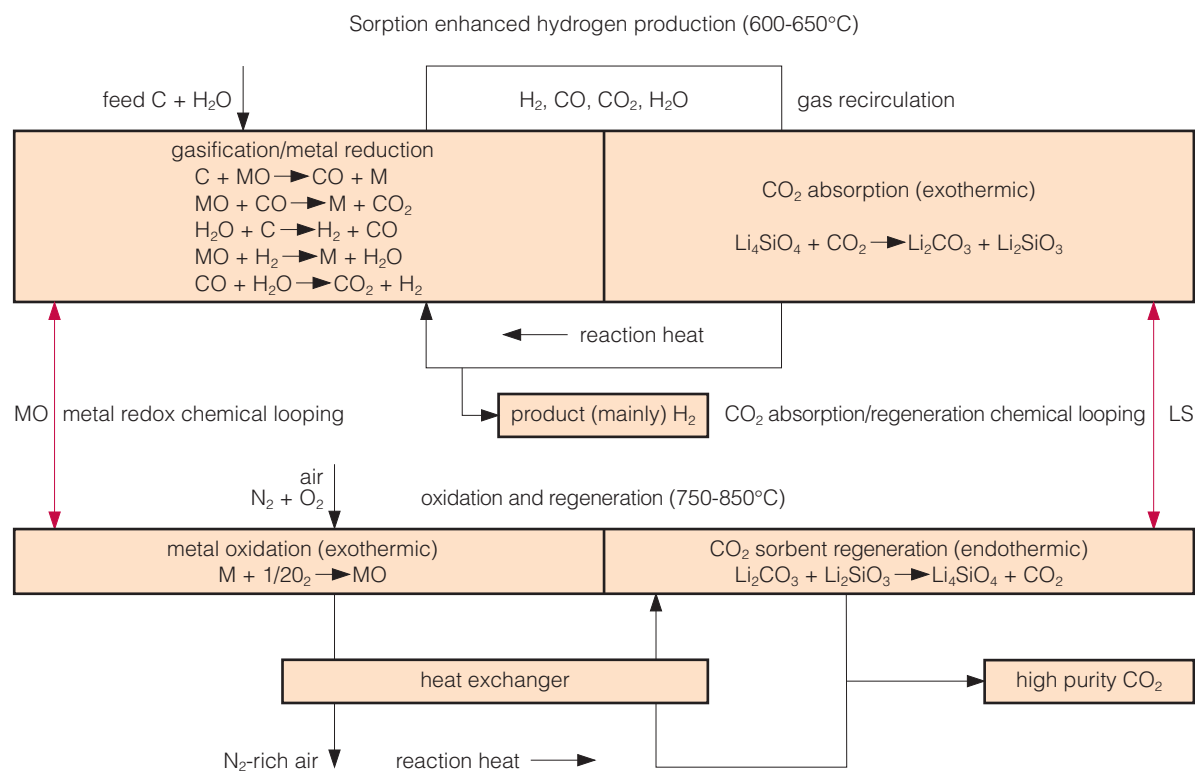
Figure 13 Advanced HyPr-RING process using chemical looping (Nakagaki, 2011)

presence of CaO. However, the CaO required in this reaction is coming from a previous step (C) where the heat for calcination is supplied by the exothermic reduction of CuO using a fuel gas. This produces a gas stream rich in CO_2 and H_2O suitable for CO_2 dehydration and compression for transport and storage. An intermediate step (B) is required for the oxidation of Cu to CuO at conditions so that the calcination of $CaCO_3$ is minimal; in order to avoid the loss of CO_2 in the stream of O_2 depleted air leaving the Cu oxidation reactor.

Hydrogen Production from Coal by Reaction Integration Novel Gasification with CO2Recovery (the HyPr-RING process) produces hydrogen from coal in a single reactor by separating CO_2 during coal gasification (Lin and others, 2005). The process involves four main reactions that are integrated in a gasifier. CaO first reacts with high pressure H_2O to form reactive $Ca(OH)_2$ and to release heat. This hydration reaction was a means of retaining the reactivity of the CaO (more on the use of hydration to retain/restore CaO reactivity can be found in Davidson (2009). The $Ca(OH)_2$ then absorbs CO_2, producing $CaCO_3$ and also releasing heat. An enhancement of the process has been devised by Nakagaki (2011) which involves a new concept of enhanced hydrogen production process including dual chemical looping, one of which separates the CO_2 from the gasification gas and the other chemical looping separates the oxygen from air. The first chemical looping is for CO_2 separation using lithium orthosilicate (Li_4SiO_4) as a solid CO_2 sorbent which can absorb CO_2 around 650°C with an exothermic reaction and regenerate around 800°C. Another chemical looping by redox reaction of a metal oxide is applied to the oxygen carrier in the gasification reactor and heat source to regenerate the sorbent. Copper oxide (CuO) is one of the suitable materials for oxygen carrier because reduction of CuO by carbon is an exothermic reaction which benefits the energy balance, while reduction of nickel oxide or haematite by carbon is endothermic. A schematic of the enhanced process is shown in Figure 13. The process is currently under development and experiment.

7   Conclusions

The consideration of hybrid capture systems is evidence that the capture of CO_2 need not necessarily be limited to the three 'conventional' strategies. However, the hybrid capture systems are mainly concepts that have not been physically studied or tested. An exception is the use of oxyfuel combustion for the calcination step in carbonate looping capture. This, though, is probably the least hybrid system of those considered.

As conceptual systems, they can offer thermodynamic advantages but there can be added complexity. So, for example, in combining post-combustion capture with oxygen enriched combustion, the reduced energy requirements for CO_2 capture is offset by the release of more reaction heat and a lower quantity of gas to exchange heat with.

As noted above, regenerable sorbents (carbonate looping) is the system that has made most headway, especially with the establishment of the 1.7 MWth La Pereda pilot plant. Again, although the thermodynamics of the system appear favourable, the plant complexity is higher than in competitive technologies such as full oxyfuel combustion or amine-based post-combustion capture.

The situation is similar when combining post-combustion capture with IGCC plant. The need for high levels of integration might lead to reduced flexibility and reduced availability of the plant. If chemical solvent capture is used then the heat needed for solvent regeneration may lead to lower efficiencies than pre-combustion capture with physical solvents.

Some of the concepts studied involve processes and components that are still under development, for example, syngas chemical looping may encounter engineering challenges. It has also been reported that, due to high capital investments and operating costs, the CO_2 avoidance costs for CLC systems have been found to be exceptionally high. But again, it has also been concluded that the energy penalties are lower compared with more conventional capture technologies.

Based on the limited number of what are largely conceptual studies a general conclusion is that, to be successful, hybrid systems must not only be thermodynamically superior but they need to avoid introducing both higher cost and increased engineering complexity. However, the existence of hybrid capture concepts means that capture systems may not have to be limited to the trinity of post-combustion, oxyfuel combustion, and pre-combustion.

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