Pre-combustion capture of CO_2 in IGCC plants

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Abstract

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. This report examines the use of pre-combustion capture in coal fuelled integrated gasification combined cycle (IGCC) plants. After the introduction there follows a short discussion of the water-gas shift (WGS) reaction. This is followed by chapters on the means of CO_2 capture by physical and chemical solvents, solid sorbents, and membranes. The results and conclusions of techno-economic studies are introduced followed by a look at some of the pilot and demonstration plants relevant to pre-combustion capture in IGCC plants.

Acronyms and abbreviations

AC	activated carbon
AGR	acid gas removal
aMDEA	activated methyldiethanolamine
BET	Brunauer-Emmett-Teller (surface area)
¢	US$ cent
c	€ cent
CaCHA	calcium chabzite zeolite
CCS	carbon capture and storage
CCU	carbon capture unit
COE	cost of electricity
db	dry basis
EDS	energy dispersive X-ray spectroscopy
EEA	extended exergy analysis
EPRI	Electric Power Research Institute
FSC	fixed site carrier
IEA	International Energy Agency
IEA GHG	IEA Greenhouse Gas R&D Programme
HCP	hypercrosslinked polymer
HHV	higher heating value
HPTGA	high pressure thermal gravimetric analyser/analysis
HSMR	hydrogen separation membrane reactor
HTC	hydrotalcite
HTWGS	high temperature water-gas shift
IGCC	integrated gasification combined cycle
LCOE	levelised cost of electricity
LHV	lower heating value
LTWGS	low temperature water-gas shift
MDEA	methyldiethanolamine
MEA	monoethanolamine
MOF	metal-organic framework
MSC	molecular sieve silica
NER	(EU) New Entrants Reserve
NETL	(US Department of Energy) National Energy Technology Laboratory
NGCC	natural gas combined cycle
OECD	Organisation for Economic Co-operation and Development
PAN	polyacrylonitrile
PBI	polybenzimidazole
PC	pulverised coal
PFC	perfluorinated compound
PSA	pressure swing adsorption
PVAm	polyvinyl amine
PVSA	pressure vacuum swing adsorption
SCPC	supercritical pulverised coal
SEM	scanning electron microscopy
SEWGS	sorbent enhanced water-gas shift
SLM	supported liquid membrane
SNG	synthetic natural gas
TBAB	tetra-n-butyl ammonium bromide
TGA	thermal gravimetric analyser/analysis
THF	tetrahydrofuran

TSA	temperature swing adsorption
UF	urea formaldehyde
WGS	water-gas shift
WGSMR	water-gas shift membrane reactor
XRD	X-ray diffraction

Contents

1 Introduction

In the Intergovernmental Panel on Climate Change special report (IPCC, 2005), pre-combustion capture is described thus:

> *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 give 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.*

With respect to carbon dioxide (CO_2) capture in an integrated gasification combined cycle (IGCC) system, post-combustion and pre-combustion technologies can be used. However, for post-combustion capture from coal-derived syngas, about 9% carbon dioxide exists in the flue gas and the partial pressure of the carbon dioxide is low. For pre-combustion CO_2 capture, the topic of this report, O_2-blown and high pressure systems are preferred because the CO_2 partial pressures are higher. This report reviews activities in pre-combustion capture carried out after the IPCC (2005) special report publication.

In a coal IGCC power plant, syngas exiting the gasifier is cleaned of particles, hydrogen sulphide (H_2S) and other contaminants and then burned to make electricity via a gas turbine/steam turbine combined cycle. The syngas is generated and converted to electricity at the same site, both to avoid the high cost of pipeline transport of syngas (with a heating value only about one third of that for natural gas) and to exploit opportunities cost-effectively for making extra power in the combined cycle's steam turbine using steam from syngas cooling.

In Figure 1, Meyer and others (2005) show the components of an IGCC that are modified for CO_2 removal. It is these components, the water-gas shift (WGS) reaction and the removal of CO_2, that form the subject of this report.

Recent IEA CCC reports have covered the other areas fairly comprehensively. These include:
- coal gasification (Fernando, 2008);
- future developments in IGCC (Henderson, 2008);
- polygeneration from coal via coal gasification (Carpenter, 2008);
- gas turbine technology for syngas/hydrogen in coal-based IGCC (Smith, 2009);
- chemical looping combustion of coal and syngas (Henderson, 2010);
- next generation coal gasification technology (Barnes, 2011).

The air separation unit has been recently examined in a report for the IEA Greenhouse Gas R&D Programme (IEA GHG) by Allam (2007, 2009). An overview of IGCC technology has also been produced by Maurstad (2005). Higman (2010) has also reviewed the application of gasification to pre-combustion carbon capture with an emphasis on the gasification technologies. The US DoE National Energy Technology Laboratory (NETL) has a comprehensive advanced carbon dioxide capture R&D programme including pre-combustion. Information about this can be found in a report by Ciferno and others (2011) and at http://www.netl.doe.gov/technologies/carbon_seq/corerd/precombustion.html.

Although this report is limited to pre-combustion carbon capture in coal-fuelled IGCCs, it is worth remembering that this is not the only option. Higman (2007b) 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

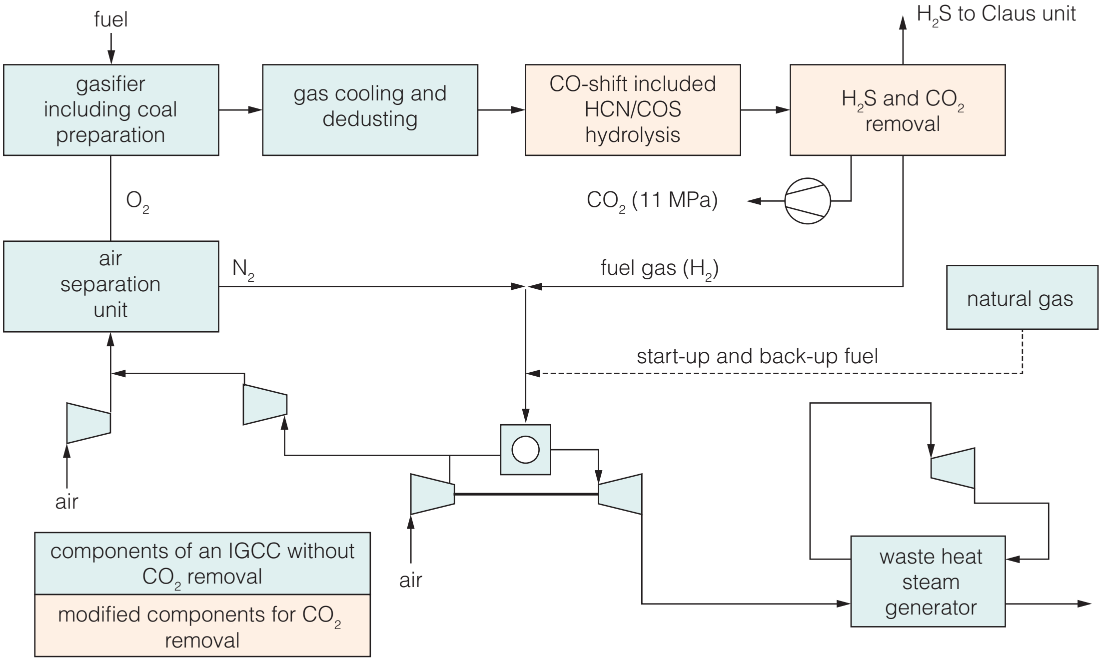


Figure 1 IGCC with CO_2 removal (Meyer and others, 2005)

dioxide is low. However, Kunze and Spliethoff (2011) have suggested that a post-combustion approach might produce a significant increase in net efficiency of 3.8 percentage points compared with a conventional IGCC plant. Another approach could be oxycombustion of the syngas such as proposed by Griffiths (2008) or Hufton and others (2011).

After this introduction there is a short discussion of the WGS reaction. This is followed by chapters on the means of CO_2 capture by solvents, sorbents, and membranes. The results and conclusions of techno-economic studies are introduced followed by a look at some of the pilot and demonstration plants relevant to pre-combustion capture in IGCC plants.

2 Water-gas shift process

The water-gas shift (CO shift conversion) or WGS process converts carbon monoxide and steam to carbon dioxide and hydrogen. The reaction

$$CO + H_2O \rightarrow CO_2 + H_2$$

consists of a slightly exothermic conversion process, and is consequently promoted at low temperatures (Cau and others, 2005a). However, low temperatures limit the rate of reaction and therefore it is necessary to use appropriate catalysts. Other parameters affecting reaction rate are pressure (up to 30 MPa, above which its effect becomes practically negligible) and steam-carbon monoxide molar ratio.

In general, two kinds of conversion process exist in industrial applications:
1. High Temperature Water-Gas Shift (HTWGS) reaction that generally takes place at temperatures in the 300–500ºC range, using iron oxides based catalysts and chromes as promoters.
2. Low Temperature Water-Gas Shift (LTWGS) reaction that takes place at temperatures in the 180–270ºC range, using metallic copper catalysts and zinc oxides and alumina as promoters and stabilisers.

The high and low temperature shift catalysts are often operated in sequence, where the high-temperature catalysts convert the bulk of carbon monoxide and the low temperature shift catalysts keep CO conversion down to ppm levels at the reactor outlet (Carbo and others, 2007). Sollai and Cau (2007) describe a laboratory test rig based on two packed-bed reactors in series to be operated at different temperatures. It was designed for testing CO-shift conversion processes using different catalysts and at varying syngas temperatures (350–500°C for the high temperature reactor and 180–250°C for the low temperature reactor) and initial syngas compositions (up to 100% of dry CO fraction).

The development of improved WGS catalysts, however, will not be discussed in this report, except to mention that a study of a commercial iron-chromium based sweet shift catalyst has recently been performed using the gas composition expected for entrained flow oxygen gasification at the Puertollano IGCC demonstration plant (Sánchez and others, 2011). Despite the high CO content in the feed gas (60 vol%, db), by choosing the right shift reactor conditions, CO concentration at the reactor outlet reached values below 3%, whereas H_2 increased up to above 50 vol% (db).

2.1 Steam requirements

The WGS unit influences the efficiency of a power plant. For a standard WGS design, the efficiency loss for an IGCC with CO_2 separation due to WGS (without having encountered any measures for separation or CO_2 compression) is in the order of 3–4%. The loss of efficiency caused by the WGS is to a major extent governed by the steam demands necessary for sufficiently high CO conversion ratios (Scherer and Franz, 2011).

Computer simulations by Raggio and others (2005; *also* Deiana and others, 2007) have indicated that the most significant parameter in the WGS conversion process is the steam/CO molar ratio. In particular, their study demonstrated that a steam/CO molar ratio equal to 2.5 is enough to achieve an almost complete CO conversion. However, this steam requirement of the WGS process is one of the efficiency penalties in pre-combustion capture. Carbo and others (2007) have pointed out that decreasing the steam requirement for the WGS reactor section provides the likeliest option to reduce the efficiency penalty. Moreover, reduction of the steam requirement enhances the operational

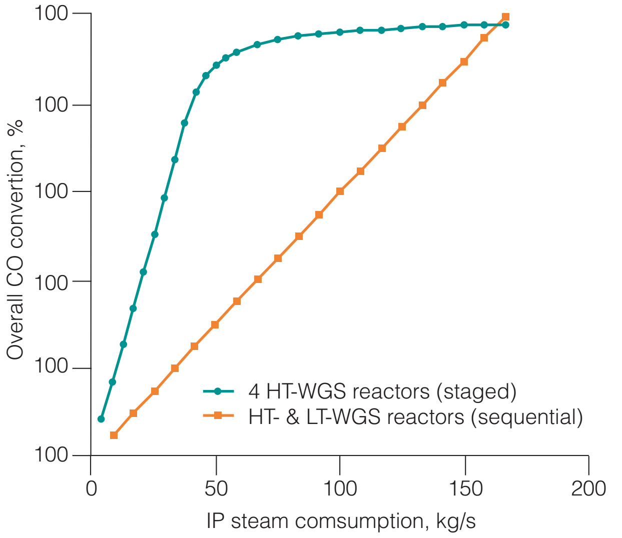


Figure 2 Overall CO conversion as a function of intermediate pressure steam conditions (dry fed gasification, conventional and advanced clean WGS section) (Carbo and others, 2007)

flexibility of the integral IGCC including CO_2 capture. Since the WGS reaction uses catalysts, the minimum steam/carbon monoxide ratio is 2, to avoid carbon deposition at the catalyst surface and formation of larger hydrocarbon molecules. However, application of the minimum steam/CO ratio of 2 results in an outlet temperature of 560°C, which results in irreversible deactivation of the catalyst by sintering. Increasing the steam supply results in a lower outlet temperature of the high-temperature shift reactor. Thus, the steam requirement of shift reactors is significantly larger than the stoichiometrically required amount of steam for CO conversion, because of catalyst requirements regarding the minimum inlet steam/CO ratio and maximum outlet temperatures. Carbo and others (2007, 2009a,b) proposed an advanced shift reactor section comprising four staged reactors with distributed syngas and quench water addition in between the reactors. The quenches were expected to result in a significant advantage: the addition of water, being both a coolant and reactant ultimately leads to a lower initial steam requirement. This advanced reactor section would reduce the steam requirement of the shift reaction up to 70% at approximately 85% CO_2 capture, in comparison with conventional shift reactor sections. A possible disadvantage is the increase in reactor volumes for the advanced shift reactor sections, which ranges from 28 to 53% in comparison with conventional shift reactor sections.

The steam requirement of the advanced shift section is significantly reduced compared with the conventional sequential shift section, when a CO conversion up to approximately 90% is required, is shown in Figure 2.

Another way of reducing the steam requirement is the use of a Sorption Enhanced Water Gas Shift (SEWGS) reactor. The SEWGS reactor is filled with high temperature shift catalyst and CO_2 adsorbent pellets. Very low CO_2 partial pressures are achieved, which enhances the shift reaction without increasing the steam requirement. This integration of sorbents and the WGS reaction will be discussed later in Section 4.10. However, the effects of operating conditions of a SEWGS unit in an IGCC power plant on the performance have been investigated by modelling and simulation by Reijers and others (2011). A countercurrent steam rinse cycle with one equalisation step was assumed. The CO_2 recovery increases with purge flow, and decreases with feed flow, cycle time and rinse flow, in order of decreasing sensitivity. The CO_2 purity is much less sensitive to changes of these conditions, except when the rinse flow or cycle time drop below a certain value. For given unit and cycle designs, the optimum cycle time and minimum steam requirements were determined with respect to the lowest efficiency penalty, with a CO_2 recovery of 90% and a dry CO_2 purity of 98% as constraints. Minimum steam/carbon ratios of 0.55 for the rinse and 1.3 for the purge gas result in the lowest efficiency penalty. Similar ratios of 0.40–0.65 for the rinse and a purge steam requirement of 1.50–1.25 (a total steam to carbon ratio of 1.90) were calculated by Wright and others (2011).

2.2 Sweet and sour

There are also ‘sweet’ and ‘sour’ shift options for the coal gas. The WGS reactor can be located either

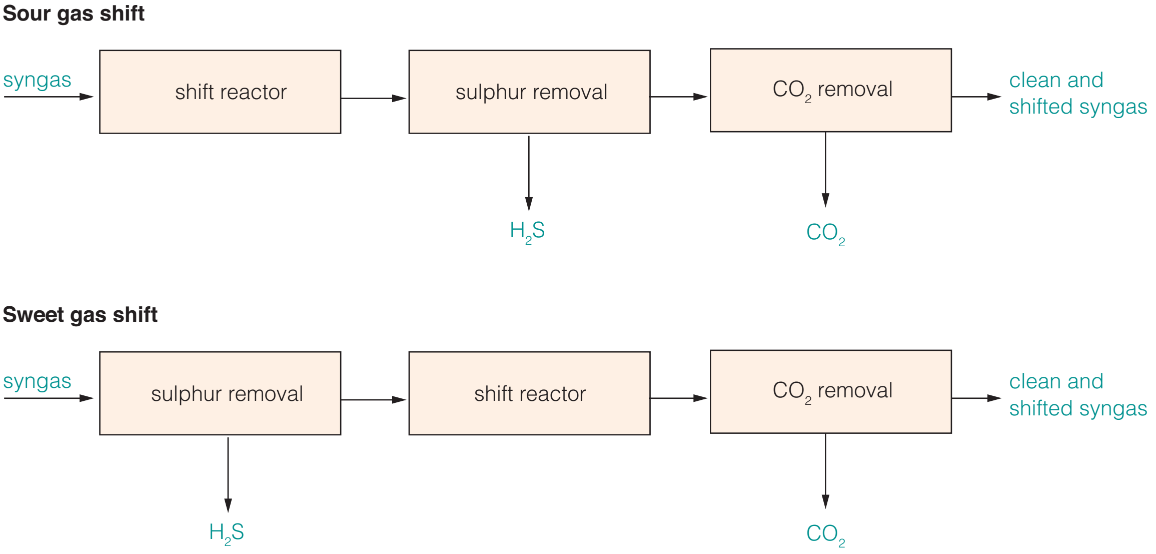


Figure 3 Sour and sweet gas shift configurations (Carpenter, 2008)

before the sulphur removal step (sour shift) or after sulphur removal (sweet shift) as shown in Figure 3. In the case of sour shift the CO_2 and the H_2S can be captured together in a single stage in, for example, a Selexol™ plant (van Aart and others, 2007). In the sour shift arrangement, the syngas, after water scrubbing, is sent to a WGS converter that uses a sulphur tolerant catalyst, more expensive than that needed in the sweet shift arrangement.

In discussing the design of an IGCC plant that could be retrofitted with carbon capture and storage (CCS), van Aart and others (2007) placed the WGS after the sulphur removal (sweet shift) to minimise the additional cost. Starr and others (2007) also suggested that, if the CO_2 is to be sent for storage, then the view is that the H_2S and the CO_2 should be removed separately.

An IGCC plant configured for a single stage of WGS and enhancement of the acid gas removal system (AGR) can achieve approximately 50% carbon capture. Studies by GE Energy (White and others, 2007) indicated that a single WGS configuration could be capable of providing carbon capture of >65%. It was concluded that the single shift configuration was well suited as a retrofit to an existing base IGCC plant. However, to achieve a maximum of 90% carbon capture, two stages of shift are needed as well as expanded AGR capacity.

In contrast, a detailed techno-economic analysis of both the Shell and GE IGCC systems found that both systems with CO_2 capture are able to benefit from the use of the sour shift option. The sour shift option avoids cooling and reheating the fuel gas before shift conversion, which results in a better process performance and lower specific investment than for the sweet shift option. Sour shift gives better process efficiency than sweet shift (Huang and others, 2007).

Even in sweet shift there may be trace quantities of H_2S present. Kinetics studies by Boon and others (2009) of the WGS reaction with a FeCr catalyst showed that 11–15 ppmv H_2S negatively affects the reaction rate. At these low concentrations H_2S does not form metal sulphides but adsorbs on the surface instead.

In order to minimise the specific steam consumption per captured amount of CO_2, application of sour WGS may be more advantageous, since the high moisture content in raw syngas can be employed to reduce the steam consumption (Carbo and others, 2009a,b). Scherer and Franz (2011) have also pointed out that sweet WGS concepts with low temperature H_2S removal cannot utilise the high water contents downstream of the gasification, hence requiring more steam addition for the WGS reaction. Therefore, sweet WGS concepts usually achieve lower efficiencies than sour WGS concepts. On the other hand, sweet WGS concepts are sometimes preferable, because the overall WGS conversion might be higher since the lower temperature range of the sweet shift favours CO conversion. As more heating value is shifted from CO to H_2, a higher recovery of H_2 is possible, which can be routed to the gas turbine.

At the Puertollano IGCC demonstration plant (*see* Section 7.1), the main finding in the sweet shift characterisation tests has been the high reactivity achieved in the first reactor of the shifting unit, near to 95% CO-CO_2 conversion. Thus, it is possible to consider a shifting process with only one step using the sweet catalyst (García Peña and Coca, 2011a,b).

2.3 WGS retrofitting

Holt (2006) has pointed out that addition of sour shift increases gas flow to the AGR particularly for dry coal fed gasifiers with high CO content. He suggested that it is unlikely that the AGR would be able to take the extra flow unless there was pre-investment oversizing. There may be a need to add a parallel absorber or replace the entire AGR plant (with a new two-column absorption system) if capture is to be added to an existing IGCC designed without capture. Alternatively the original AGR (focused on H_2S removal) could be retained and a sweet shift added after the AGR with a simpler bulk CO_2 removal system added after the shift. This would minimise intrusion into existing plant. This trade-off between sour versus sweet shift needs to be examined and may differ among the gasification technologies. Sweet shift may incur additional efficiency and output penalties.

Alderson and others (2007) have pointed out that the insertion of a shift converter into an existing IGCC plant with no shift would mean a near total rebuild of the gasification waste heat recovery, gas treatment system, and the heat recovery steam generator, with only the gasifier and gas turbine retaining most of their original features. This raises the question of whether the conversion of an existing IGCC plant to capture CO_2 is really a retrofit operation. Higman (2007a) has commented that each design of base plant will require a different approach to retrofitting. It would seem that there is no standard way of retrofitting IGCC plants. This is not, however, likely to be a problem given the low number of existing plants that could be retrofitted.

After a retrofit there can be a loss of MWth and mass in the resulting gas turbine fuel (Kubek and others, 2007). The exothermic WGS reaction means that less fuel energy is available to fire the gas turbine. Also the higher specific heat of H_2 versus CO means less mass flow in the fuel stream (by ~50%). The combined impact results in 5–10% less power output from the gas turbine depending on the magnitude of the shift.

3 Solvents

When discussing CO_2 capture in IGCC plants, 'conventional' capture processes usually refer to capture using physical solvents. Physical solvent capture is a mature, commercial process used in gasification plants but not, as yet, in IGCC plants. Commercial physical solvent processes for CO_2 removal are often used as benchmarks with which other capture technologies can be compared.

3.1 Physical solvents

Because the CO_2 partial pressure of the shifted syngas is up to 1000 times higher than that of the flue gas in post-combustion capture, in pre-combustion capture it can be preferable to use different solvents, known as physical solvents, which combine less strongly with CO_2. The advantage of such solvents is that CO_2 can be separated from them in the stripper mainly by reducing the pressure, resulting in much lower energy consumption (Davison and Thambimuthu, 2009).

Cau and others (2005b) analysed the performance of an advanced zero-emission power plant based on a stoichiometric hydrogen-oxygen combustion steam turbine cycle, integrated with coal gasification and physical absorption and liquefaction of carbon dioxide. The syngas from the gasifier composed mainly of H_2, CO, CO_2 and H_2O, is converted in a CO-shift reactor to redistribute the chemical energy of the CO into H_2, obtaining CO_2. The high partial pressure of the CO_2 was particularly favourable for physical absorption so the CO_2 was then captured using Selexol™, a mixture of polyethylene glycol dimethylethers. CO_2 removal is also favoured by low temperature, which increases CO_2 solubility in the solvent but requires the gas to be contaminant-free. Thus, the CO_2 removal section was placed downstream from the syngas conditioning section in which the sulphur compounds (mainly H_2S) are removed from the syngas in an absorption tower using the same physical solvent used for CO_2 removal. H_2S and CO_2 could be removed together in a single absorption column. However, as this would complicate disposal of the CO_2-H_2S mixture, two separate columns are preferable. The use of Selexol™ for CO_2 capture in gasification plants has been presented by Palla (2009) stressing that it is a proven, commercial technology.

Another physical solvent is the Rectisol® wash process which can remove H_2S and COS as well as CO_2 from synthesis gas using methanol as the solvent. Methanol has a high selectivity for the removal of these gases compared with H_2 and CO. In physical wash processes the required flow rate of the solvent is inversely proportional to the feed gas pressure thus the process economics improves with increasing gas pressure. The Rectisol® wash process is usually operated at low temperature levels of –35°C or –60°C requiring external refrigeration. At the higher CO_2 partial pressure found in coal gasification gases, methanol recirculation rates of Rectisol® washes are much lower than for chemical (amine) wash systems resulting in lower power, steam, and cooling water consumption (Kaballo and Kerestecioglu, 2006; Kauf and Kerestecioglu, 2007; Prelipceanu and others, 2007). Unlike amines, corrosion is not an issue for Rectisol®.

Since both the conventional physical solvents for CO_2 removal require cooling and subsequent reheating of the stream before the gas turbine in an IGCC plant, this decreases the plant thermal efficiency and thus increases the overall costs. Consequently, there is an opportunity for the development of alternative processes which should be economical and absorb carbon dioxide without significant cooling of the humid gas streams (Pennline and others, 2008). The objective would be to find physical solvents for selective CO_2 capture from post-water-gas-shift reaction streams under elevated pressures and temperatures that are representative of gasification conditions.

Higman (2010) has pointed out that, despite physical solvents having a higher capital cost than amine washes, the lower steam consumption and superior selectivity are probably the principal reasons behind what is ultimately an economic decision. The fact that physical washes can deliver part of the CO_2 at an elevated pressure, thus reducing CO_2 compression costs, also contributes to their attractiveness in this service.

Perfluorinated compounds

Heintz and others (2005; *see also* Pennline and others, 2006, 2007, 2008) carried out an extensive literature review and found that perfluorinated compounds (PFCs) have low reactivity and high chemical stability due to the high energy of their C-F bonds. They have high boiling points and low vapour pressures because of the strength of the C-F bond and high molecular weight. They also have no dipole and very low molecular interactions due to the repulsive tendency of fluorine atoms. These properties lead to high gas solubility, low vapour losses, and low forces required for expelling the gas molecules upon decreasing pressure or increasing temperature. Thus, PFCs show a high potential for selective CO_2 capture from post-shift fuel gas streams at elevated pressures and temperatures.

They devised an experimental programme to obtain the equilibrium gas solubility and the hydrodynamic and mass transfer parameters for CO_2 and N_2 in three different PFCs, namely perfluoro-perhydrofluorene ($C_{13}F_{22}$), perfluoro-perhydrophenanthrene ($C_{14}F_{24}$), and perfluoro-cyclohexylmethyldecalin ($C_{17}F_{30}$) – PP10, PP11, and PP25 respectively. The equilibrium solubilities of CO_2 and N_2 in PP10, PP11, and PP25, expressed as a mole fraction, appeared to increase with pressure at constant temperatures. The solubilities for both gases were greater in PP25 than in the other two PFCs. Under similar operating conditions, the solubility of CO_2 in the three PFCs appeared to be about seven times that of N_2, which was attributed to the closeness of the solubility parameter of CO_2 to those of the PFCs when compared with that of N_2. The results showed that CO_2 is more soluble in the Selexol™ solvent than in the PFCs only at low temperatures (⩽60°C). However, the Selexol™ solvent would be less effective at higher temperatures typifying those at the exit of the gasifier system in a warm gas clean-up application. The study revealed the thermal and chemical stability and the ability of the PFCs to absorb CO_2 selectively at temperatures up to 227°C and pressures as high as 3 MPa.

One aspect of the work with PFCs where improvement could be made was in the vapour pressure of these solvents. Accordingly, the focus of the physical solvent research was switched from fluorinated solvents to ionic liquids, which have characteristically negligible vapour pressures, even at elevated temperatures such as those used in IGCC warm gas cleaning (Pennline and others, 2008).

Ionic liquids

Ionic liquids are ionic, salt-like materials that are liquid below 100°C. Ionic liquids tend to have good solvent properties and are miscible with water or organic solvents. Screening experiments on ionic liquids as solvents for CO_2 have been reported by Pennline and others (2008).

Oligomers

Selexol™, a mixture of polyethylene glycol dimethylethers, is an oligomeric CO_2 solvent. The solubility of CO_2 in four physical solvents was reported by Miller and others (2009). The oligomers studied were polyethyleneglycol dimethylether (PEGDME), perfluoropolyether (PFPE) that has a perfluorinated propyleneglycol monomer unit, polydimethyl siloxane (PDMS), and polypropyleneglycol dimethylether (PPGDME). These oligomers had 2–5 repeat units. The four oligomers were assessed for capturing CO_2 from high pressure streams. The pressure required to dissolve a specified amount (wt%) of CO_2 in the PFPE-CO_2 pseudo-binary system was found to be far greater than that required by the three other solvents, PPGDME, PEGDME, and PDMS. This was unexpected, given that fluorous polymers are widely known to have lower miscibility pressures in CO_2 than nonfluorous analogous solvents. The performance of PPGDME, PDMS, and PEGDME were comparable: therefore it was concluded that they were promising solvents for CO_2 physioabsorption.

The viability of several other oligomeric CO_2-philic solvents was studied by Miller and others (2010).

They compared their CO_2 absorption, hydrophobicity, and viscosity with the commercial Selexol™ solvent. The solvents tested included the four previously studied together with polypropyleneglycol diacetate (PPGDAc), polybutyleneglycol diacetate (PBGDAc), polytetramethyleneetherglycol diacetate (PTMEGDAc), and glyceryl triacetate (GTA). When compared with Selexol™, the candidate solvent should absorb more CO_2, absorb less water, have lower viscosity, exert a lower vapour pressure, and have the capability of being less costly when manufactured in large volumes. Overall, PDMS and PPGDME were found to be the best oligomeric solvents tested. They exhibit properties that make them very promising alternatives for the selective absorption of CO_2 from a mixed gas stream, especially if the absorption of water is undesirable. Relative to Selexol™ or PEGDME, PDMS exhibited comparable CO_2 absorption, lower viscosity, and complete immiscibility with water. Relative to Selexol™ or PEGDME, PPGDME exhibited comparable CO_2 absorption, comparable viscosity, and dramatically greater hydrophobicity (only 2–3 wt% water dissolves in PPGDME at 22–40°C).

3.2 Chemical solvents

Chemical solvents, as proposed for post-combustion CO_2 capture, have also been considered for pre-combustion capture. In the design for the Sotacarbo pilot plant, the chosen process of CO_2 capture used absorption of carbon dioxide with a solution of water and monoethanolamine (MEA) at an operating temperature of about 30°C, in an advanced reactor, developed by Ansaldo Ricerche, which uses two innovative membranes for the gas diffusion in the liquid phase and for the liquid/gas separation downstream of the absorption process (Amorino and others, 2007a,b; Deiana and others, 2007). However, the gasifier is designed to operate with oxygen-enriched air rather than oxygen, resulting in a syngas containing ~40% nitrogen (N_2) so the separation of the CO_2 after the WGS reaction is not simply the separation of CO_2 and H_2. A detailed description of the whole experimental equipment, together with an analysis of the first experimental results obtained for every plant section has been provided by Maggio and others (2009). A CO_2 separation efficiency up to 85–90% has been obtained without solvent recirculation.

Tomizaki and others (2010a) have pointed out that chemical solvent absorption methods need increased temperatures (>120°C) and reduced CO_2 pressures to recycle the CO_2 absorption solvent efficiently. This is because all the common alkanolamine based solvents have a relatively high heat of reaction and tend to hold CO_2 tightly even at low CO_2 partial pressures. There is a need for chemical sorbents that have lower heats of reaction and greater differences in CO_2 solubility between CO_2 rich and lean solutions at CO_2 pressures close to one another (~2 MPa). This would allow the use of low grade or waste heat to and also maintain the CO_2 partial pressure level during the processes, thus saving energy and cost. Previously, Tomizaki and others (2008) had identified imidazole derivatives as potential candidates for capture and release of CO_2 in the range of partial pressures from 1 to 4 MPa. Later (Tomizaki and others, 2010a), the heats of reaction and vapour-liquid equilibria for *N*-methyldiethanolamine and some novel absorbents were studied. Based on these measurements, 1,2-dimethylimidazole and 4-(2-hydroxyethyl)morpholine (both tertiary amines) were found to be promising candidates for absorption and recovery of CO_2 with partial pressures of 1.6 MPa or higher without loss of the CO_2 pressure level. It was also reported that quantitative ^{13}C nuclear magnetic resonance spectroscopy could be used to obtain CO_2 solubility data and also identify the inorganic carbon species in aqueous amine solvents (Tomizaki and others, 2010b). The solubilities determined were in good agreement with those determined by vapour-liquid equilibria over a wide pressure range. In all the solutions the amounts of physically absorbed CO_2 increased with pressure and were 15–30% of the total CO_2 at 40°C and 4 MPa.

In Australia, the CO2CRC has developed a hot carbonate solvent absorption process based upon work completed in the laboratory and using ASPEN simulation. The Mulgrave Capture Project solvent pilot plant (*see* Section 7.1), with the capacity to capture 1 tonne per day of CO_2 from synthesis gas, has been built to demonstrate this technology. The use of boric acid as a rate activator is a promising environmentally benign and lower cost alternative to amine based activators. The performance of the pilot plant with and without boric acid was determined as part of the work. The performance of the solvent pilot plant is summarised in Table 1. Operation of the pilot plant was not optimised during the first campaign due to significant operational issues, such as solvent precipitation and pump malfunction. Upon overcoming these issues during the second campaign, it was possible to optimise process temperatures such that more CO_2 was absorbed and the energy usage of the reboiler was reduced. The impact of the boric acid was insignificant and was thought to be because the reaction rate is not limiting the absorption of CO_2 at the high temperature of operation.

The most significant operating issues that were encountered during the operation of the pilot plant were:

1 the absorber water balance:
2 impurities absorbed into the solvent from the synthesis gas.

If the synthesis gas is saturated or under-saturated with water, a net loss of water from the solvent will occur resulting in a more concentrated solvent, a greater risk of bicarbonate precipitation and level control problems. The impurities absorbed into the solvent from the synthesis gas were liquid hydrocarbons and coal dust from a filter candle failure. The liquid hydrocarbons slightly altered the physical properties of the solvent, such as surface tension but caused more significant problems when combined with the coal dust to form larger sticky particles. In the absence of an inline solvent filtering system, these sticky particles caused a range of operational issues such as pump strainer blockages and heat exchanger fouling.

Table 1 Summary of results for the three campaigns of the Mulgrave capture project (Anderson and others, 2011)

CASE	Promoter	Syngas flowrate, kg/h	Absorber temperature, °C	CO_2 removed, %	Reboiler energy usage, MJ/kgCO_2
Campaign 1	None	325	80	38	8.2
Campaign 1	None	300	90	56	6.4
Campaign 1	Boric acid	300	95	56	6.0

Table 2 Technical advantages and challenges for pre-combustion solvent technologies (Ciferno and others, 2011)

Advantages	Challenges
CO_2 recovery does not require heat to reverse a chemical reaction	CO_2 pressure is lost during flash recovery.
Common for same solvent to have high H_2S solubility, allowing for combined CO_2/H_2S removal	Must cool down synthesis gas for CO_2 capture, then heat it back up again and re-humidify for firing to turbine
System concepts in which CO_2 is recovered with some steam stripping rather than flashed, and delivered at a higher pressure may optimise processes for power systems.	Low solubilities can require circulating large volumes of solvent, resulting in large pump loads
	Some H_2 may be lost with the CO_2

Another carbonate-based process is being developed by SRI International as part of a NETL research programme (Ciferno and others, 2011). The process is based on the use of a high capacity and low cost aqueous solution containing ammonium carbonate, which reacts with CO_2 to form ammonium bicarbonate. The bicarbonate solution is heated to release the CO_2 and regenerate the carbonate solution. Ammonium carbonate has high net CO_2 loading, is a low cost and readily available reagent, and requires little solvent make-up. Bench-scale experiments have demonstrated an efficient absorption of CO_2 and H_2S at elevated pressures without the need for sub-ambient operation. High pressure CO_2 and concentrated H_2S streams can be released during the regeneration of loaded solution.

3.3 Comments

Although solvents are used successfully in coal gasification plants, they are not, as yet, used in IGCC plants. The main obstacle is probably the need to cool the gas to allow CO_2 capture followed by heating it up again for firing the IGCC gas turbine. This decreases the plant thermal efficiency and thus increases the overall costs. A summary of the advantages and challenges related to pre--combustion solvents has been produced by Ciferno and others (2011) and is presented in Table 2.

4 Solid sorbents

The use of solid sorbents in post-combustion carbon dioxide capture has been discussed in detail in an IEA CCC report by Davidson (2009). Solid sorbents have also been considered for pre-combustion carbon capture. However, there are different conditions to be considered. Siriwardane and others (2005b) have noted that CO_2 removal at warm gas temperatures (200–350°C) is the most energy efficient for IGCC systems to prevent loss of thermal efficiency due to cooling of the gas. However, at the time of writing in 2005, no regenerable sorbents for CO_2 removal at these temperatures had been reported in the literature. Also, the performance of sorbents such as zeolites can be adversely affected in the presence of steam.

4.1 Activated carbons

Drage and others (2009a) have suggested that activated carbon (AC) adsorbents are ideally suited for CO_2 capture after the WGS reaction where CO_2 is at high pressure and 'physical' adsorbents with weak basic functionalities are required for CO_2 capture, as opposed to the strong basic functionalities required at low pressures.

Blackman and others (2006) have pointed out that activated carbons have higher CO_2 capacity at pressures above atmospheric. Their relatively moderate strengths of adsorption for gases also facilitate desorption. A number of novel AC adsorbents with a range of surface areas were evaluated including ACs prepared from phenolic resin, urea formaldehyde (UF) resin and polyacrylonitrile (PAN). It was found that, although the equilibrium uptakes were heavily dependent on sample pre-treatment and increased with degassing under high vacuum, the novel ACs displayed considerably higher equilibrium capacities than existing commercial ACs. With no pre-treatment, adsorption capacities ranged from below 5% to over 50% at 4 MPa and correlated well with micropore surface area. An activated PAN with a surface area of 3000 m^2/g had the highest uptake and pre-treatment by high vacuum degassing increased its capacity to 100%. Adsorption isotherms obtained at 150°C and 170°C demonstrated that at least two-thirds of the CO_2 could be removed by temperature swing adsorption (TSA). The AC adsorbents had higher capacities that were much higher than existing physical solvent absorption systems and the CO_2 could be desorbed at relatively high pressure with a consequent saving on compression costs.

A wide range of AC adsorbents for pre-combustion capture has been explored by Drage and others (2006). Adsorption isotherms generated from the differential pressure apparatus demonstrated adsorption to be rapid, with approximately 80% of the equilibrium uptake being achieved in seconds, and the final equilibrium uptake reached after about four minutes. It was found that the CO_2 uptakes at high pressure correlated well with micropore surface area. Regeneration has been demonstrated by both thermal and pressure swing techniques (TSA and PSA). It was concluded that thermal swing regeneration has excellent potential in that over two thirds of the adsorption capacity can be regenerated whilst retaining pressure, therefore saving on the high energy penalties associated with re-compression of the gas. Both techniques offer good adsorption, and potential advantages over the current solvent absorption systems. The high pressure AC adsorbents are advantageous due to their ease of regeneration and potential to keep CO_2 at high pressures, thus avoiding the energy penalty associated with re-compression. Nine carbons with tailored textural properties were developed and produced using a phenolic resin as precursor material. These carbons were tested for CO_2 adsorption at high pressures (pre-combustion CO_2 capture). A maximum CO_2 adsorption capacity of 58 wt% (13 mmol/g) at 3 MPa was attained. In addition, the carbons showed high selectivity to CO_2 with maximum H_2 uptakes of 0.3 wt% (Drage and others, 2009a). Drage and others (2009b) also reported that the capacities of the ACs ranged from 1.5 to over 11.6 mmol/g (6.6–51 wt%) at 4 MPa, with no special pre-treatment, and correlated well with the micropore volume. The highest uptake was produced from AC3000, an activated carbon with a Brunauer-Emmett-Teller (BET) surface area of in excess of 3000 m^2/g. However, when the adsorption capacity is considered on a volumetric basis, phenolic resin derived carbons have comparable adsorption capacities.

In order to obtain highly microporous carbons with suitable characteristics for the separation of CO_2 and H_2 under high pressure conditions, Resol and Novolac phenolic resins were synthesised by Martín and others (2009). The prepared phenolic resins were carbonised at different temperatures and then physically activated with CO_2. Tested carbons showed increased CO_2 uptakes at higher pressures (up to 3 MPa) and high selectivity towards CO_2. At atmospheric pressure, the highest CO_2 uptake was 9.6 wt%, whereas at high pressure, the maximum uptake of 39.2 wt% was reached. These values were later reported as 10.8 wt% at atmospheric pressure and up to 44.7 wt% at 2.5 MPa (Martín and others, 2011a,b). The addition of ethylene glycol up to 1 wt% had resulted in an enhancement of the textural development due to the lower temperatures of carbonisation and activation with CO_2.

The limits of CO_2 capture capacity of carbons have been studied by Martín and others (2010, 2011a,b). They found that the CO_2 capture capacity is essentially a micropore filling process and not adsorption on the surface. Micropore volume and average micropore width are the only factors controlling the equilibrium CO_2 capture performance of carbons. Thus, carbon sorbents behave differently under post- and pre-combustion conditions. Under post-combustion conditions (0.1 MPa and 25°C), absorption involves only the smaller micropores of carbon; carbons should have high micropore volume from pores below 0.6 nm. Under pre-combustion conditions (2 MPa and 25°C), absorption occurs by the filling of the entire microporosity; carbons should have pore sizes centred in the supermicroporosity range (1.5–2 nm). Overall, it was concluded that a realistic CO_2 uptake limit of 10–11 wt% was realistic for post-combustion capture but, for pre-combustion capture, this could rise to, but not exceed, 60–70 wt%.

Preliminary results of an ongoing study to develop activated carbons for CO_2 pre-combustion capture have been presented by Ogbuka and others (2011). Three activated carbons were synthesised using zeolites as template with the aim of producing high surface area and pore volume adsorbents for application in gasification. Acetylene gas was used as the chemical vapour deposition (CVD) agent. The physical properties were evaluated and related to the materials CO_2 adsorption capacity, determined using thermogravimetric analysis at ambient pressure. A maximum CO_2 adsorption capacity of 2.35 mmol/g (10.3 wt%) was recorded, and the dependence of adsorption capacity on material micropore volume and surface area was established.

4.2 Zeolites

Zeolites (aluminosilicate molecular sieves) are suitable candidate sorbents for removing carbon dioxide (CO_2) from high pressure fuel gas streams; however, the systems would be even more energy efficient if the sorbents were operational at moderate or high temperatures, such as the gas streams from IGCC systems (Siriwardane and others, 2005a). Five manufactured zeolites were tested but the CO_2 adsorption capacities of the zeolites were significantly lower at 120ºC than at ambient temperature. The two zeolites with the highest adsorption capacities had the largest pore diameters and the highest Na/Si ratios. Volumetric gas adsorption tests of CO_2 and nitrogen on the two zeolites were conducted at 120°C, up to a pressure of 2×10^6 Pa. Both showed high CO_2 adsorption capacity at high pressure. High pressure flow reactor studies also indicated the preferential adsorption of CO_2 from gas mixtures at 120°C. CO_2 adsorption rates were measured by thermogravimetric analysis, and the rates were similar for the two zeolites.

The use of zeolite 13X has been considered by Xiao and others (2009) based on vacuum/pressure swing absorption technology. The process involves two separate stages – water removal and carbon dioxide capture. Both stages operate at 250°C. The H_2 product gas contains less than 1% water vapour. The technical feasibility of the process was evaluated using a numerical simulator. It could achieve 97.7% CO_2 purity and 91.3% recovery.

Singh and others (2009) found that zeolites are only effective CO_2 adsorbents in the temperature range 90–250°C. The optimum temperature for 13X is approximately 120°C beyond which it loses its capacity, while calcium chabazite zeolite (CaCHA) retains its capacity up to 200°C. Zeolites 13X and CaCHA adsorb considerable amounts of water and in the absence of a thermal influence require very deep vacuum to regenerate the zeolite. In the presence of water, the CO_2 capacity is significantly reduced. Zeolite 13X loads ammonia strongly at 120°C and a TSA cycle is required for desorption. However, H_2S loading appears to be reversible under the temperature conditions studied. The adsorption/desorption of H_2S and NH_3 on CaCHA was also studied using a thermal gravimetric analyser (TGA) and the opposite behaviour to 13X was observed. Thus CaCHA strongly loads H_2S at the temperatures studied (200°C), and does not load ammonia. 13X and CaCHA zeolites exhibited stable cyclic capacity over the temperature range investigated. Adsorption/desorption of CO_2 was found to be rapid (on the order of seconds). However, in the presence of moisture, H_2S or NH_3 the CO_2 capacity is substantially diminished. Hence the practical application of these materials to an IGCC process will require pre-treatment of the syngas to remove the impurities, or use of a multi-layered bed in which an appropriate pre-layer is inserted to accommodate the impurities.

The CO2CRC/HRL Mulgrave pilot plant (*see* Section 7.1) included the construction of a fully automated cyclic adsorption gas separation apparatus that can operate in either single-bed or dual-bed adsorption mode. Two 1 m long adsorption columns were packed with 200 g of zeolite 13X in the centre of the column and both ends of the column were packed with zeolite 3A to protect the adsorbents from contaminants including moisture. The adsorbents were calcined before use. Four different pressure vacuum swing adsorption (PVSA) processes were designed and performed. Processes with pressure equalisation and product purge showed higher CO_2 concentration. The results showed a trade-off between CO_2 concentration and recovery. Numerical simulation studies validated from the experimental results indicated that it was possible to produce 99% CO_2 at 120°C under optimised process conditions. Engineering issues identified included presence of heavy hydrocarbons on the adsorbent as well as trace amounts of sulphur. Adsorbent technology must be able to accommodate these impurities.

More details of the performance of the adsorbents have been provided by A Lee and others (2011). Various adsorbents were prepared and their performance at high temperature was studied. Zeolite 13X and calcium chabazite showed good breakthrough results at temperatures of less than 200°C due to their reasonably high absorption capacity and fast kinetics. Results of PVSA of zeolite 13X showed that it was possible to produce CO_2 up to 98% in concentration at 120°C and 200°C with the presence of a pressure equalisation step followed by product purge steps. CO_2 concentration results without these steps reached only 80.5% and 69.8% at 120°C and 200°C, respectively. However, contamination may be a serious issue for use of adsorbents in syngas applications. It was found that the colour of the zeolite 3A from the top layer of the column was changed after approximately 24 hours operation. Scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS) revealed up to 20 wt% carbon in the sample.

4.3 Magnesium double salts

Singh and others (2009) have found that magnesium double salts present very favourable carbon dioxide isotherms and demonstrate significant carbon dioxide loading and the isotherms are suitable for PSA or TSA operation at high temperature. They prepared Mg-Na double salts and K-Mg double salts. Mg double salts operate in a high temperature range, and exhibit very high adsorption capacity and selectivity for CO_2. It was found that they are extremely promising candidates for high temperature capture although difficulties were in producing reproducible samples. At 300°C, a Mg-Na double salt sample showed excellent adsorption capacity, which is however lost on repeated cycling and required reactivation to 400°C. At 400°C adsorption was still present but reduced. There appeared to be a combination of chemisorption and physisorption leading to an ‘optimal’ operating temperature which is approximately 375°C. H_2S was adsorbed but not desorbed under purge regeneration. Na and K-Mg double salts show a very high cycling CO_2 capacity in a very narrow temperature range (375–400°C) indicating significant PSA cyclic potential. However, strong adsorption of H_2S will require protection or thermal regeneration. It is also not currently known what the effect is of water on the CO_2 capacity of double salt materials.

4.4 Hydrotalcites

Hydrotalcites (HTCs) are layered double hydroxides of general formula $Mg_6Al_2(CO_3)(OH)_{16}\ 4H_2O$. Their use has been proposed by Xiao and others (2009) based on vacuum/pressure swing absorption technology. The technical feasibility of the process was evaluated using a numerical simulator. It could achieve 97.2% CO_2 purity and 94.8% recovery. However, for some gas turbines there is a limit on the water concentrations entering the turbine (~13%) and this constraint may not be achieved using hydrotalcite.

HTCs operate in a high temperature range, and exhibit very high adsorption capacity and selectivity for CO_2. It does not appear that water influences their operation. TGA experiments using 1% H_2S in helium and 1% NH_3 in helium were conducted on HTC materials by Singh and others (2009). Regeneration was attempted by physical purge (not thermal means) to see if it was possible to utilise a pressure wing adsorption cycle. H_2S is strongly adsorbed to HTC and is not desorbed under purge regeneration. Thus thermal means will be needed to regenerate HTC if it is to be used in IGCC conditions. Cycling experiments on HTC materials suggested they perform very well in the temperature range 300–400°C, however, significant chemisorption and reduction in capacity over time were observed.

CO_2 sorption measurements at 250°C on hydrotalcites with lateral platelet sizes from 20 nm to 2 µm were performed by Meis and others (2010). The samples were activated by heating in N_2 at 500°C to remove CO_2 and water. Unsupported hydrotalcites showed an invariant and low capacity as a function of platelet size of ~0.1 mmol/g (0.44 wt%). An increase by a factor of 10–25 in HTC weight based capacities to 1.3–2.5 mmol/g (5.7–11 wt%) was accomplished by supporting the HTCs on carbon nanofibre. This higher capacity of activated supported samples was tentatively related to a higher density of low-coordination oxygen (edges and corners) in the $Mg(Al)O_x$ phase crystal interacting with the carbon nanofibre surface.

Tests carried out by A Lee and others (2011) have shown that hydrotalcite showed very slow desorption kinetics due to the chemisorption of CO_2.

4.5 Porous crystals

Organic crystalline solids have been proposed for multicomponent gas separation by Thallapally and others (2007). Several classes of organic solids (including clathrates) are stable at high temperatures (>250°C) and their cage/pore properties can be tailored to target guest molecules. They can be produced in engineered structures, such as thin films, membranes, or microporous materials. No covalent or ionic chemical bonds are involved – gas separation and retrieval cycles can be performed without degradation of the host. In preliminary research, reasonably good mass loadings were measured for CO_2 with multiple compounds. It was concluded that all the data so far suggest that continued research will unlock the potential of these materials for combined high pressure, high temperature CO_2 separations.

Clathrate hydrates

Clathrate hydrates (or gas hydrates) are crystalline water-based solids physically resembling ice, in which small non-polar molecules (typically gases) are trapped inside ‘cages’ of hydrogen-bonded water molecules. Most low molecular weight gases, including H_2 and CO_2, will form hydrates at suitable temperatures and pressures. Clathrate hydrates are not chemical compounds as the sequestered molecules are never bonded to the lattice, in part justifying their inclusion in this chapter on solvents. Clathrate hydrate crystallisation has been studied as means of capturing CO_2 by Linga and others (2007a,b). They found that, when a gas mixture of CO_2 and H_2 forms gas hydrates the CO_2 prefers to partition in the hydrate phase. In fact, very small amounts of H_2 were found in the hydrate. This provides the basis for the pre-combustion capture of CO_2 from a fuel gas mixture. Using a model fuel gas mixture, hydrates were formed at 0.6°C since it had been decided to form hydrate crystals from liquid water and not from ice. Hydrate formation pressure increases with temperature and in order to minimise compression costs the smallest possible pressure is desired. The minimum pressure to form hydrate crystals from the fuel gas at 0.6°C was found to be 5.1 MPa. Experiments were carried out at 7.5 MPa and 8.5 MPa, 2.4 MPa and 3.4 MPa respectively above the hydrate equilibrium pressure of 5.1 MPa. The difference between the experimental pressure and hydrate equilibrium pressure is considered as the driving force of the hydrate formation. Experiments showed that CO_2 recovery was 42.5% and 36.1% at 7.5 and 8.5 MPa, respectively. The decrease in recovery from 7.5 to 8.5 MPa can be explained by the fact that, at the higher pressure, H_2 gas competes with carbon dioxide for cage occupancy which results in lower occupancy of carbon dioxide in the hydrate phase. The hydrates obtained at both pressures contained more than 85% CO_2. It was suggested that, with the addition of a second stage, it would be possible to obtain a hydrate phase containing more than 95% CO_2.

The use of a second stage is considered a weak point by Seo and Kang (2010) since it reduces the economics of the separation process. They noted that hydrate formation in confined structures such as silica gel pore structures shows a higher formation rate and enhanced fractionation effect than in the bulk water phase. The possibility of implementing silica gels in the hydrate-based CO_2 separation process, especially in pre-combustion capture, was proposed. Laboratory-scale studies of hydrate formation from 41 mol% CO_2 and balanced H_2 gas mixture showed that most of the cages are occupied by CO_2 molecules, and that a 98.7 mol% CO_2 and balanced H_2 gas mixture is retrieved from the dissociation of hydrate formed at ~9.2 MPa and 274.15 K. When decreasing the pressure from 9.2 MPa to 6.0 MPa, the concentration of CO_2 in the hydrate phase decreases from 98.7 to 96.5 mol%, which is a tendency opposite to that in bulk water.

Additives have also been studied as a means of improving hydrate formation. The effect of tetrahydrofuran (THF) concentration on separation of CO_2 from CO_2/H_2 gas mixture via hydrate crystallisation was investigated by H J Lee and others (2010). The induction time generally decreased with increasing the amount of THF addition as well as with increasing the hydrate formation driving force. The concentration of THF and the hydrate formation driving force were found to influence the occupation of the cavities by the individual CO_2 and H_2 gases. Based on the kinetic experiments, it was found that 1.0 mol% THF was the optimum concentration.

The effects of tetra-*n*-butyl ammonium bromide (TBAB) on the separation and/or collection of CO_2 from CO_2/H_2 (40:60) gas mixture via hydrate crystallisation was investigated by Kim and others (2011). The phase equilibrium conditions shifted to milder conditions as the amount of TBAB additive increased up to 3.0 mol%. The existence of a critical concentration of the additive on the phase equilibrium conditions was also observed. The hydrate formation rate in a 1.0 mol% TBAB solution showed the highest value while the hydrate formation rate in a 3.0 mol% TBAB solution showed the lowest value. The phase equilibrium temperature of CO_2/H_2 (40:60) mixture gas hydrate systems with the TBAB additive were in the range of 283 and 290 K at the IGCC process pressure range of 2.5–5.0 MPa. The effects of TBAB were also studied by X-S Li and others (2011a). Their results indicated that the increase of the TBAB concentration or the driving force can enhance the separation efficiency, except when the TBAB concentration is above 0.29 mol% or the driving force is above 2.50 MPa. At these limits it was possible to obtain a 96.85 mol% CO_2-rich gas and an 81.57 mol% H_2-rich gas. Approximately 67% of CO_2 is recovered in the hydrate process. Hence, X-S Li and others (2011a) proposed a conceptual process that consists of a single-stage hydrate process in conjunction with a membrane separation stage to capture CO_2 and H_2, taking advantage of high selectivity (hydrate crystallisation) and small size (membranes).

The effect of the presence of cyclopentane (CP) in the TBAB solution was investigated by X-S Li and others (2011b). Their results showed that the volume of the TBAB has an effect on the CO_2 separation and the induction time, and the addition of the CP into the TBAB solution enhances the CO_2 separation and shortens the induction time. A system with the CP/TBAB solution volume ratio of 5 vol% and TBAB solution/reactor effective volume ratio of 0.54 was found to be the optimum to obtain the largest gas uptake and the highest CO_2 separation efficiency at 274.65 K and 4.0 MPa. Compared with the results with tetrahydrofuran (THF) as an additive, the gas uptake was enhanced by at least two times and the induction time was shortened by at least ten times at similar temperature/pressure conditions. In addition, the CO_2 concentration in the decomposed gas from the hydrate slurry phase reached approximately 93 mol% after the first stage separation at 274.65 K and 2.5 MPa. Gas uptakes of more than 80 mol% were obtained after 400 s at a temperature range of 274.65–277.65 K and a pressure range of 2.5–4.5 MPa.

Metal-organic frameworks

Metal-organic frameworks (MOFs) are crystalline compounds of metal ions or clusters coordinated to organic molecules to form one-, two-, or three-dimensional structures that can be porous. Their potential for use in post-combustion CO_2 capture was reviewed by Davidson (2009). Their use in pre-combustion CO_2 capture by high pressure CO_2/H_2 separation has been briefly reported by Herm and others (2011a,b). Their data suggest that coordinatively unsaturated metal sites in the pores of adsorbents are beneficial for this separation, and studies of other materials with this property are under way. It was estimated that it was possible to obtain CO_2/H_2 selectivities between 2 and 860 and mixed-gas working capacities, assuming a 0.1 MPa purge pressure, as high as 8.6 mol/kg (37.8 wt%) and 7.4 mol/litre.

4.6 Organic polymers

Hypercrosslinked polymers (HCPs) synthesised by copolymerisation of *p*-dichloroxylene (*p*-DCX) and 4,4′-bis(chloromethyl)-1,1′-biphenyl (BCMBP) constitute a family of low density porous materials with excellent textural development. Such polymers show microporosity and mesoporosity and exhibit BET surface areas of up to 1970 m^2/g. The CO_2 adsorption capacity of these polymers was evaluated using a thermogravimetric analyser (atmospheric pressure tests) and a high pressure magnetic suspension balance (high pressure tests) by Martín and others (2011c). CO_2 capture capacities were found to be related to the textural properties of the HCPs. The performance of these materials to adsorb CO_2 at atmospheric pressure was characterised by maximum CO_2 uptakes of 1.7 mmol/g (7.4 wt%) at 298 K. At higher pressures (3 MPa), the polymers showed CO_2 uptakes of up to 13.4 mmol/g (59 wt%), superior to zeolite based materials (zeolite 13X, zeolite NaX) and commercial activated carbons. In addition, these (relatively inexpensive) polymers showed low isosteric heats of CO_2 adsorption and good selectivity towards CO_2. It was concluded that HCPs have potential to be applied as CO_2 adsorbents in pre-combustion capture processes where high CO_2 partial pressures are involved.

4.7 Functionalised solid sorbents

A steam tolerant sorbent based on polar organic liquids (amines, glycols, and ethers) trapped inside the unit layers of a clay has been developed by NETL (Siriwardane and others, 2006; *also* Siriwardane and Robinson, 2006). This sorbent showed stable sorption performance at 40ºC and at atmospheric pressure during a 25-cycle test, and regenerability at 80–100ºC. The presence of steam and 20 ppm of SO_2 did not appear to affect the performance of the sorbent. The sorbent was prepared for both fixed and fluidised bed applications. The CO_2 removal efficiency of the sorbent was 99%, and it has a CO_2 capture capacity of 3.6 moles/litre (2.1 mol/kg, 9.2 wt%) obtained at 40ºC. This CO_2 capture capacity value corresponded to a delta loading (amount of CO_2 that could be recovered when the sorbent is regenerated at 100ºC in the presence of CO_2) value of 2.8 moles/litre (~7.2 wt%) which is close to the minimum acceptable value based on the specific heat capacity of the clay support. When the CO_2 concentration was increased to 28%, the CO_2 capture capacity increased. The capture capacity of the sorbent at 2 MPa is significantly higher than that of the Selexol™ process, which has a capture capacity of less than 1 mole/litre in similar conditions. Since the sorbent performed well at high pressure and with a high concentration of CO_2, it was suggested that it would be suitable for separation of CO_2 from IGCC coal gas after the shift reactor to produce H_2.

4.8 Solid chemisorbents

A review of reversible chemisorbents for carbon dioxide and their potential applications including the WGS reaction and removal of CO_2 from flue gas has been produced by K B Lee and others (2008).

Li and others (2005) have listed the requirements for sorbents for pre-combustion carbon capture. They should be effective at high temperature for effective integration with other high temperature syngas cleaning technologies. Additional requirements include:
- regenerable;
- high purity, high pressure CO_2 by-product;
- highly tolerant to syngas contaminants (for example, sulphur);
- effective across wide range of CO_2 concentrations;
- suitable for both fixed or fluidised bed applications.

A screening programme revealed that lithium orthosilicate was a potential candidate:

$$\underset{\text{(ortho)}}{Li_4SiO_4} + CO_2 \leftrightarrows Li_2CO_3 + \underset{\text{(meta)}}{Li_2SiO_3}$$

Testing showed that it was:
- effective in multiple gases, particularly sulphur-containing syngas;
- regenerable;
- stable in multicycle performance.

Effective promoters were identified and bench-scale testing results were described as promising.

High temperature carbon dioxide removal from synthesis gas (produced from coal gasification) using solid regenerable sorbents has been tested by Hussein and others (2007). The experimental work involved initial adsorption/desorption tests for lithium orthosilicate and hydrotalcite based sorbents in nitrogen and carbon dioxide gas mixture using a thermal gravimetric analyser (TGA). Adsorption capacities as a function of temperature were measured along with desorption characteristics using both temperature swing and inert gas purging. The potassium carbonate promoted hydrotalcite sample had total carbon dioxide sorption capacities as high as 0.89 mol/kg (3.9 wt%) in the temperature range of 400–500ºC. Multicycle studies indicated rapid degradation of capacity (~27%) in first three cycles and stabilisation afterwards at an adsorption capacity of ~0.5 mol/kg (2.2 wt%). For the lithium orthosilicate, the sorption reaction took place at temperatures as low as 400°C but the rate and amount of sorption was low. The sorption rate and weight uptake increased with temperature up to 700°C. The temperature affects the sorption rate both kinetically and thermodynamically. It also showed good desorption properties at 800°C in a combination of temperature swing and inert purge process. Additional multicycle tests were conducted which showed excellent reproducibility with constant working capacity of ~4 mol/kg (~17.6 wt%). It was concluded that the lithium silicate sample is effective in the temperatures between 600°C and 700°C, but it requires carbon dioxide partial pressures of >0.2 atm (~20 kPa).

Siriwardane and others (2005b, 2007c,d) reported tests on a sodium based sorbent (a 1:2 weight ratio of NaOH/CaO) at 315°C with both simulated IGCC fuel gas and simulated post-shift gas reactor gas. They found a CO_2 removal efficiency of >99% and the CO_2 capacities improved during a ten cycle test. Its capacity was more than 3 moles/kg (13.2 wt%) in the presence of steam. The sorbent could be regenerated at 700°C. Rehydroxylation was found to be very important after regeneration and is more favourable at lower temperatures. When water vapour was not introduced to the sorbent after regenerating at 700°C, the reactivity during the subsequent cycle was very low. Thus, rehydroxylation is critical for retaining the reactivity during cyclic tests. Heat of reaction data indicated that the reaction during the first cycle was primarily due to the reaction with NaOH. A novel sodium-based sorbent was also reported by Siriwardane and others (2007d) which was able to capture CO_2 (5–7 moles/kg; 22–31 wt%) at 600°C and 1 atm; it was possible to regenerate the sorbent at 885°C and 1 atm. The performance was stable over a multicycle test. This sorbent was also able to enhance the WGS reaction to produce H_2 without a catalyst. However, regeneration of these sorbents requires high temperatures because it involves the decomposition of the alkali carbonates formed during absorption. The high regeneration energies of these sorbents would result in significant loss in system efficiency. Therefore, it is necessary to find a low energy regeneration procedure to be able to use CO_2 removal sorbents effectively (Siriwardane and others, 2011). The effect of various additives on the decomposition of sodium carbonate (Na_2CO_3) was evaluated using temperature-programmed desorption, thermogravimetric analysis, X-ray diffraction, and X-ray photoelectron spectroscopy. Incorporation of additives, CaO and $Ca(OH)_2$, had a significant effect on lowering the decomposition temperature of Na_2CO_3, while $CaCO_3$, SiO_2, and Al_2O_3 had no effect. For both CaO and $Ca(OH)_2$ the initial decomposition temperature of Na_2CO_3 decreased from 785°C to 550°C. However, $Ca(OH)_2$ had a more pronounced effect than that of CaO, with the concentration, flow rate of sweep gas, and heating rate all significantly affecting the decomposition temperature of Na_2CO_3. The formation of a carbonate-type intermediate in the presence of CaO and $Ca(OH)_2$ may have promoted the decomposition of Na_2CO_3.

Abbasian and others (2005; *also* Hassanzadeh and Abbasian, 2010) reported that, by using magnesium oxide based sorbents, carbon dioxide can be removed from raw coal gas in the temperature range of 350–550°C at 1–5 MPa. These temperature and pressure ranges closely match those expected in IGCC processes, including high temperature WGS operation, enhancing hydrogen production in IGCC processes. A total of sixty-two different sorbents were prepared. The sorbents were prepared by either various sol-gel techniques (22 formulations) or modification of dolomite (40 formulations). In general, the modified dolomite sorbents had significantly higher magnesium content, larger pore diameter and lower surface area, resulting in significantly higher reactivity compared with the sol-gel sorbents. Some of the dolomite sorbents were modified by the addition of potassium carbonate to the half-calcined dolomite through wet impregnation method. The estimated potassium content of the impregnated sorbents was in the range of 1-6 wt%. Hassanzadeh and Abbasian (2010) noted that the addition of a potassium based promoter is essential to increase the reactivity of the MgO based sorbents.

Testing in a high pressure thermal gravimetric analyser (HPTGA) revealed that none of the sol-gel sorbents was suitable for CO_2 removal in IGCC processes. The results of HPTGA tests with modified dolomite indicated that the reactivity and the overall capacity of modified dolomite sorbents were at least one order of magnitude higher than those of the sol-gel based sorbents. The results of the tests conducted with various dolomite-based sorbents indicated that the reactivity of the modified dolomite sorbent increases with increasing potassium concentration, while higher calcination temperature adversely affects the sorbent reactivity, which should be attributed to higher extent of agglomeration at higher temperatures. The results also indicated that, as long as the absorption temperature is well below the equilibrium temperature, the reactivity of the sorbent improves with increasing temperature (350–425°C). As the temperature approaches the equilibrium temperature, the rate of CO_2 absorption decreases due to the significant increase in the rate of reverse regeneration reaction. The regeneration reaction can be performed either at higher temperatures (>450°C) or at lower pressures in a CO_2-free environment.

The results of cyclic tests showed that the reactivity of the sorbents gradually decreases in the cyclic process. To improve the long-term durability (reactivity and capacity) of the sorbents, the sorbents were periodically re-impregnated with the potassium additive and calcined. The results indicated that, in general, re-treatment improves the performance of the sorbent and that the extent of improvement gradually decreases in the cyclic process. The presence of steam significantly enhances the sorbent reactivity and significantly decreases the rate of decline in sorbent deactivation in the cyclic process.

Magnesium-based sorbents have been tested in a laboratory-scale reactor at 200–250°C at ~1 MPa with 28% CO_2 in He saturated with steam (Siriwardane and others, 2006, 2007a,b,d). Regeneration was conducted at 375°C and ~1 MPa. A ten-cycle flow reactor test conducted at 250 h^{-1} space velocity with about 3 g of magnesium based sorbent indicated that the sorbent has a very high CO_2 capture capacity (4 moles/kg, 17.6 wt%). Further testing revealed that an increase in pressure and/or H_2O concentration resulted in improved CO_2 capture capacity. It was suggested that such sorbents offer great promise for IGCC applications. The high capacities will contribute to low regeneration cost and small vessel size. The regeneration temperature of the sorbent is 375°C, and the temperature swing from absorption to regeneration is very low. High pressure regeneration is advantageous because the CO_2 compression costs required for sequestration can be reduced. A novel sorbent consisting of $Mg(OH)_2$ was developed by Siriwardane and Stevens (2009) for CO_2 capture at 200–315°C. Thermodynamic analysis indicated that the $Mg(OH)_2$ sorbent system is highly favourable for CO_2 capture up to 400°C at ~3 MPa. $MgCO_3$ formed during sorption decomposes to release CO_2 at temperatures as low as 375°C up to ~2 MPa. MgO rehydroxylation to form $Mg(OH)_2$ is possible at temperatures up to 300°C at ~2 MPa. The experimental data showed that the sorbent is regenerable at 375°C at high pressure and that steam does not affect the sorbent performance. A multicycle test conducted in a high pressure fixed bed flow reactor at 200°C with 28% CO_2 showed stable reactivity during the cyclic tests. The capture capacity also increased with increasing pressure. The sorbent exhibits a high CO_2 capture capacity of more than 3 mol/kg (13.2 wt%) at 200°C with an efficiency of CO_2 capture of ~99%. X-ray diffraction (XRD) analysis of the CO_2 exposed sorbent indicated the presence of crystalline $MgCO_3$ but the spectrum was still dominated by $Mg(OH)_2$ peaks. This was attributed to bulk $Mg(OH)_2$ being inaccessible to the gaseous CO_2 during capture, suggesting that the sorbent's capacity could be further improved if its structure were opened up to allow greater permeability of CO_2. Fourier transformation infrared (FTIR) spectroscopy showed that two carbonate species were formed during CO_2 capture (Fisher II and Siriwardane, 2011). Bridged carbonate reached a maximum concentration after ten minutes whereas the bidentate carbonate intensity continued to increase. Correlating the IR data to the bench-scale data indicates the bidentate carbonate formation continues after the usable capture capacity is reached. Further investigation on how to promote the rate of formation of bidentate carbonate will be pursued. Increasing the rate of formation of bidentate carbonate would effectively increase the usable capture capacity, possibly reaching capture capacity above 90%.

Dasgupta and others (2008) looked at designing calcium oxide (CaO) sorbents that would yield materials with higher reactivity and capacity by altering their morphology by use of surfactants while maintaining their reactivity over repeated cycles of carbonation and calcination. Study of the literature suggested that mean pore sizes greater than 3.2 nm would be less susceptible to pore pluggage and thus provide higher conversion even with lower total surface area. Morphologically altered high surface area CaO precursors were synthesised using a precipitation method. Cationic surfactants were used to increase the mean and median particle size and anionic surfactants to decrease the mean particle size. In addition, the mean pore size and pore distribution were also strongly affected by the surfactant. The synthesised sorbents were compared with commercial CaO. CO_2 uptake by commercial CaO was less than 40% and decreased monotonously from an initial value of 52% to nearly 20% after 11 cycles. On the other hand, the uptake by the laboratory synthesised samples showed nearly 100% conversions with only a 5% decrease after 50 cycles. The reactivities of the synthesised removal agents were found to be greater than ten times that of the commercially available calcium based sorbents.

Florin and Harris (2008) also observed enhanced conversion for CaO derived from precipitated $CaCO_3$ and nanosized $CaCO_3$, compared with CaO derived from commercially available (micrometre sized) $CaCO_3$. The superior performance was attributable to a porous structure that was less susceptible to diffusion resistances, and thus a high rate of conversion was maintained beyond the kinetically controlled phase.

A new synthesis method to obtain mixed $CaO/Ca_{12}Al_{14}O_{33}$ (mayenite) solids for high temperature CO_2 capture was presented by Mastin and others (2011). The modification of a pure phase $Ca_3Al_2O_6$ solid through a thermal treatment under controlled conditions leads to a high CO_2 absorption capacity material, with very promising long-term stability during absorption/desorption cycles. The sorbent possessed a high CO_2 absorption capacity – up to 20 gCO_2/100 g sorbent – with a total conversion of 90%, during more than 140 carbonation/calcination cycles at 870°C with 50 vol% steam in CO_2. This was attributed to the formation of CaO nanoparticles on the surface of larger Ca/Al mixed oxides particles during the thermal treatment. Additionally, the total absorption capacity of the sorbent could be increased up to 30 gCO_2/100 g sorbent by increasing the CaO-to-$Ca_3Al_2O_6$ weight ratio in the initial composition without loss of reactivity and durability.

Regenerable solid sorbents have been considered for use in sorbent enhanced water-gas shift (SEWGS) and this will be discussed in Section 4.10.

4.9 Sorbents in the coal gasifier

From an exercise in screening CO_2 absorbing materials, Feng and others (2007) calculated that CaO is thermodynamically and kinetically the best candidate among metal oxides for CO_2 capture in a coal gasifier. They identified a region within which high purity H_2 can be produced from carbon gasification: the molar ratio of water to carbon has to be over 4, the pressure between 1 and 11 atm, and the temperature between 700 and 930 K. The pressure has to be low to reduce the amount of CH_4 formed, and the temperature has to be low to reduce the amounts of CO and CO_2.

Berger and others (2005) presented a steam gasification process for clean conversion of biomass or lignite in one step in a fluidised bed that used in situ CO_2 separation using CaO (lime) as the bed material. However, one of the challenges identified was the cycle stability of the sorbent material (mechanical, chemical), crucial for process economics.

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. A continuous reactor system that contained feed mechanism, a solid-gas contact area, and equipment for supplying heat and pressure and for separating gases and solids was built. Coal/CaO mixtures were continuously supplied to a flow-type reactor, where they were allowed to react with high temperature, and high pressure steam. Product gases were separated from the solid residues using a cyclone and a filter, and were continuously analysed. It was found that H_2 was the main product gas (>80%) and that a small amount of CH_4 was also produced.

Corella and others (2006) have studied steam gasification of coal with CO_2 capture in a fluidised bed. They noted that calcined limestone (CaO) intervenes in the overall gasification reaction network in at least five different types of reactions. The effectiveness of the CaO for CO_2 capture in the coal gasifier is, therefore, affected/influenced by the other four simultaneous or competitive types of reactions in the gasifier. The reactions involving CaO are:

- absorption of CO_2 to produce $CaCO_3$;

- catalysing the steam reforming and dry elimination of tar producing coke which can deactivate the CaO;
- reacting with other inorganic species to produce inactive calcium species;
- sintering after a number of calcination/carbonation cycles;
- formation of CaS, if the coal has a high sulphur content.

The reactions involving tar mean that CaO works much worse in gasifiers than in combustors. It was calculated that the ratio of CaO to coal needed to be between 2 and 80 kg of CaO/kg of coal. The effects of gasifier temperature were also considered. The most often found and/or used temperature for coal gasification in a fluidised bed is 850–900°C. However, when combined with CO_2 capture by CaO, MgO, or similar sorbents, the gasification temperature has to be relatively low, between 600°C and 720°C, because of the equilibrium limitations. A gasification gas with an H_2 content as high as 80 vol% (db) was obtained by gasification of coal with pure steam at 600–800°C by Corella and others (2008). The gasifier used was an atmospheric and bubbling fluidised bed operating with CaO in the bed as the CO_2 sorbent. The research was carried out at a small pilot plant-scale with continuous feeding of coal and batch mode introduction of the CaO. To capture CO_2 at atmospheric pressure, the gasification with in-bed CaO had to be carried out at low-medium (600–800°C) gasification temperatures. For this reason, the tar content in the gasification gas was high (up to 52 g/m^3), which lowered the value of the H_2 rich gasification raw gas. It was demonstrated that a gas rich in H_2 (80 vol% H_2, db), and with very low CO_2 and tar contents, can be obtained only if the coal gasification, at atmospheric pressure and with pure steam, is carried out at CaO/coal ratios above 10–15. As soon as the CaO became deactivated, after about one hour in the facility, due to the CO_2 and to the coke forming on its surface by several simultaneous causes, the composition of the gasification raw gas became the same as that typically obtained when silica sand or another not very active solid is used as bed material in the gasifier.

A research project on the upgrading of high moisture low rank coal to hydrogen and methane (CH_4) was performed by Hawthorne and others (2008) – the C2H upgrade process. The process consisted of two core reactors:

1. a steam gasifer with in situ CO_2 capture by CaO, and
2. a sorbent regenerator with the possibility to produce a separate CO_2 stream.

In general, the sorbent CO_2 capacity decreased over multi cycling due to the changes of pore structure and sintering. The H_2 content in the gasification gas increases as the mass fraction of CaO fed with the fuel increases (up to 15 wt% CaO was fed). The tar content at a bed temperature of 650°C was around 10–12 g/m^3 during the CO_2 capture phase which was considered to be too high to be a 'useful' product gas unless further tar reduction processes were employed. The investigators concluded that the final solution of the C2H gasification process was to work continuously at high, above ~20 CaO/coal ratios. A continuous process, with a CaO/coal ratio above 20, would allow hot CaO (>900°C) to come into contact with gasifier product gas and further reduce the tar content making the gas usable for downstream processing. The CaO 'purge' from the C2H process could be used as a raw material substitute (a pre-calcined feed) in cement production. This would allow savings of fuel (66%) and CO_2 emissions (88%) since most of the energy required in cement production is required for the highly endothermic calcination reaction of limestone. It was concluded that the C2H based IGCC process is economically competitive compared with

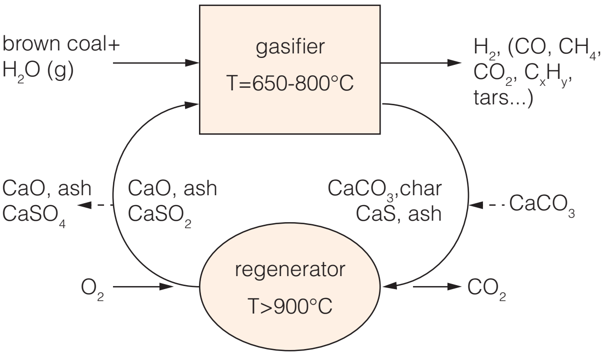


Figure 4 Lime Enhanced GaSification (LEGS) process (Weimer and others, 2008)

Table 3 Solid streams in the LEGS process related to 100 kg lignite input (Weimer and others, 2008)

Stream	Amount, kg
Purge	34.0 (0.061%)
CaO input gasifier Ash input gasifier $CaSO_4$ input gasifier	410.9 60.2 52.3
Solid input gasifier, total	523.4
$CaCO_3$ make-up	47.7

conventional IGCC systems, especially for CO_2 capture: the specific investment cost was estimated at <1500 €/kWe and the CO_2 mitigation cost was <20 €/t CO_2 avoided.

A similar process is described by Weimer and others (2008) which they call the LEGS process (Lime Enhanced GaSification). A general scheme is shown in Figure 4. It was recognised that the utilisation of the solid purge in cement production imposes restrictions on the purge composition with respect to ash and sulphur content. Material balance calculations of the core process show that the required solid purge of the sorbent cycle is mainly attributed to the necessary removal of ash and $CaSO_4$ if the solid purge is used as a pre-calcined feedstock for cement production. The decay in the CaO capture capacity over many calcination-carbonation cycles demands a high sorbent circulation ratio but does not dictate the purge fraction. The solid streams in the gasifier related to 100 kg lignite input were calculated and are given in Table 3. It was suggested that the integrated cement production has the intrinsic advantage that improvement of sorbent cycle stability is not as crucial compared with other lime based approaches such as HyPr-RING process.

Southern Illinois University developed a reaction swing process for the separation of hydrogen from syngas constituents and impurities such as CO, CO_2 and H_2S (Wiltowski and others, 2008). The main reactions in this process are the conversion of CO to CO_2 by disproportionation on a catalyst and subsequent removal of the CO_2 by a suitable CO_2 removal agent. CaO was determined to be the most suitable CO_2 removal agent. In the hydrogen enrichment mode, the coal gasification products are passed through a bed of Fe_2O_3. Three major reactions take place:

- CO is oxidised to CO_2;
- CO disproportionation via the Boudouard reaction resulting in carbon deposition and CO_2 formation;
- steam reforming of CH_4.

The products are then passed through the bed of CaO to remove the carbon dioxide. The process was applied to simultaneous coal gasification and hydrogen enrichment in a single reactor. It was found that, at 650°C, a Fe_2O_3:coal ratio of 22:1 and a Fe_2O_3:CaO ratio of 1:2 resulted in effective gasification and over 99% pure hydrogen stream. Multiple enrichment-regeneration cycles were also conducted. The efficiency of separation did not decrease as a result of the enrichment-regeneration cycle.

A reactor configuration for hydrogen generation through coal/CaO/steam gasification with inherent carbon dioxide separation has been proposed by Chen and others (2011). It has been simulated using Aspen Plus software. The results of the simulation indicated that, at atmospheric pressure, the hydrogen purity can reach 96 vol% at a steam flow of 80 mol/s and CaO recycle rate of 30 mol/s when the carbon conversion rate is 0.50. Increasing the steam flow and CaO recycle rate can enhance the hydrogen yield and purity. It was found that there is no advantage in increasing the pressure – in fact, an increase in system pressure has a negative impact on hydrogen yield and purity. In the simulation, the methane yield increases from 0.1 to 1 MPa, which directly impairs the hydrogen purity. More importantly, higher pressure results in a higher calcination temperature for CaO regeneration. At 1 MPa, the calcination temperature is approximately 1100°C. At such a high temperature, the CaO sorbent is easily deactivated. It was noted that, in a practical application, sintering and deactivation of sorbents is inevitable over multiple cycles, leading to the decay in CO_2 capture. Therefore, the factual CaO recycle rate would be higher than the theoretical calculation to ensure a sufficient CO_2 capture capacity.

4.10 Sorbent enhanced WGS

Gauer and Heschel (2005) have pointed out that the thermal stability of solid sorbents allows the sorption process to be integrated into the conversion of carbon monoxide (CO) to CO_2 in the water gas shift (WGS) reaction. They also noted that, at temperatures of 300°C and above, chemical sorbents are superior to physical adsorbents since they have approximately one order of magnitude larger capacity. The most promising sorbents were identified as calcium and lithium compounds with lithium mixed oxides apparently the better choice if the energy for CO_2 desorption and compression is taken into account. As discussed in Chapter 2, the WGS reaction is an exothermic equilibrium. If integrated with CO_2 capture, the equilibrium changes such that there is increased CO conversion. At least 90% of the CO is converted up to 450°C if the sorbent is lithium orthosilicate (Li_4SiO_4). Even higher conversions can be achieved with CaO but its regeneration consumes more energy. Conventional WGS processes are carried out with steam ratios of $H_2O/CO \geqslant 3$ to promote CO conversion of approximately 80%. In the presence of Li_4SiO_4, a steam ratio of 1.5 is theoretically sufficient to convert 95% and raising the pressure to 2.5 MPa could result in complete conversion. However, it was found that pure Li_4SiO_4 was not suitable for fast CO_2 capture in the temperature region of the WGS reaction. This could be improved by doping with iron, resulting in increased CO_2 absorption from about 500°C as well as enhanced desorption. Nevertheless, sorbent deterioration for Fe-doped Li_4SiO_4 was still evident; after five sorption/desorption cycles, the initial capacity was reduced to 85%.

A calcium oxide based sorbent is used in the Zecomix project (Calabrò and others, 2005, 2006, 2007, 2008; Carapelluci and others, 2005, (*see* Section 7.1). The Zero Emission COal MIXed technology concept combines two different systems: the Zero Emission Coal gasification and the Zero Emission Combustion TEChnology based on hydrogen fuelled internal combustion turbine cycle. The ZECOMIX plant would integrate a gasification unit, which is characterised by coal hydrogasification and carbon dioxide separation, with a power island, where a high hydrogen content syngas is burnt with a pure oxygen stream. The proposed plant has four sections:

- coal gasification island;
- CO_2 capture unit;
- calciner island;
- power plant.

In hydrogasification, the coal reacts to form methane. In the carbon capture unit there is a simultaneous process of reforming of methane to CO and H_2 followed by the WGS reaction and CO_2 capture from coal syngas. This process was named TSSEMR (thermal swing sorption enhanced methane reforming). Calabrò and others (2007) stress that the comprehension of the gas solid reaction is a crucial key for evaluating the reaction rate value and the activity for CO_2 capture. The sorbent chosen for use in the ZECOMIX process was dolomite and a mathematical model for its uptake of CO_2 was developed by Stendardo and others (2007; Stendardo and Foscolo, 2009). Calabrò and others (2008) have calculated that the plant, equipped with a CO_2 capture unit could reach an efficiency close to 50%. However, Romano and Lozza (2010) have shown that, unless CaO exiting the plant could be used as by-product, low CaO utilisation is consequently highly detrimental to plant performance.

CaO was used to absorb CO_2 as a means of enhancing hydrogen production in the WGS reaction by Iyer and others (2006). However, they observed that the performance of the high temperature shift

(HTWGS) iron oxide catalyst and calcium oxide system towards H_2 production deteriorates over multiple cycles due to the deactivation of the HTWGS catalyst by the CO_2 gas that is evolved during the high temperature calcination phase. The active phase of the HTWGS catalyst is magnetite (Fe_3O_4). However, in the presence of an oxidising atmosphere, such as pure CO_2, the magnetite phase gets oxidised to the haematite (Fe_2O_3) form during the calcination step. This could be avoided by pre-treating the oxidised catalyst to a reducing H_2/H_2O mixture at 600°C which reduces the haematite back to the active magnetite. Combining this with the WGS reaction and carbonate looping was found to produce high purity hydrogen with in situ CO_2 capture.

Laboratory performance tests of a material prepared in the form of small pellets with cores made of calcium and magnesium oxides and shells made largely of alumina impregnated with a nickel catalyst were carried out by Satrio and others (2007). These showed that CO, CH_4, and toluene, which are representative products of gasification, were largely converted to H_2 by reacting the material with steam in the presence of the catalyst/sorbent, so that CO_2 was absorbed as it was produced. The sorbent was easily regenerated by raising its temperature, which made it possible to reuse the catalyst/sorbent repeatedly. It was recognised that for the water gas shift reaction (with no methane reforming) that the pellets would not require a separate catalyst so they do not need to be impregnated with the nickel.

Calcium oxide was used as the sorbent in a study of sorbent enhanced WGS reaction by Shamsi (2008). The CaO sorbent was tested for WGS activity with and without a WGS catalyst (0.4%Pt/Ce_2O_3) as shown in Figure 5. The results showed that the sorbent was acting as a catalyst during the reaction. The CO conversion was much higher than for the inert materials, but did not perform as well as the WGS catalyst alone.

NETL researchers have developed novel CO_2 capture sorbents for the moderate temperature application of the WGS reaction (Stevens and others, 2009). The sorbents were evaluated for their ability to enhance the WGS reaction at temperatures of 300–600°C, both in the presence and absence of catalyst. The sorbents were based on calcium oxide (CaO) and sodium hydroxide (NaOH) as a promoter, at ratios of 4:1, 10:1, and 20:1, respectively, by weight. A pure calcium oxide sorbent was also employed in the study as a baseline. Testing at 500–600°C in the absence of catalyst resulted in CO conversions of nearly 100% prior to sorbent saturation, surpassing the thermodynamic equilibrium CO conversion of the gas-phase WGS reaction under identical conditions. The sorbents were also

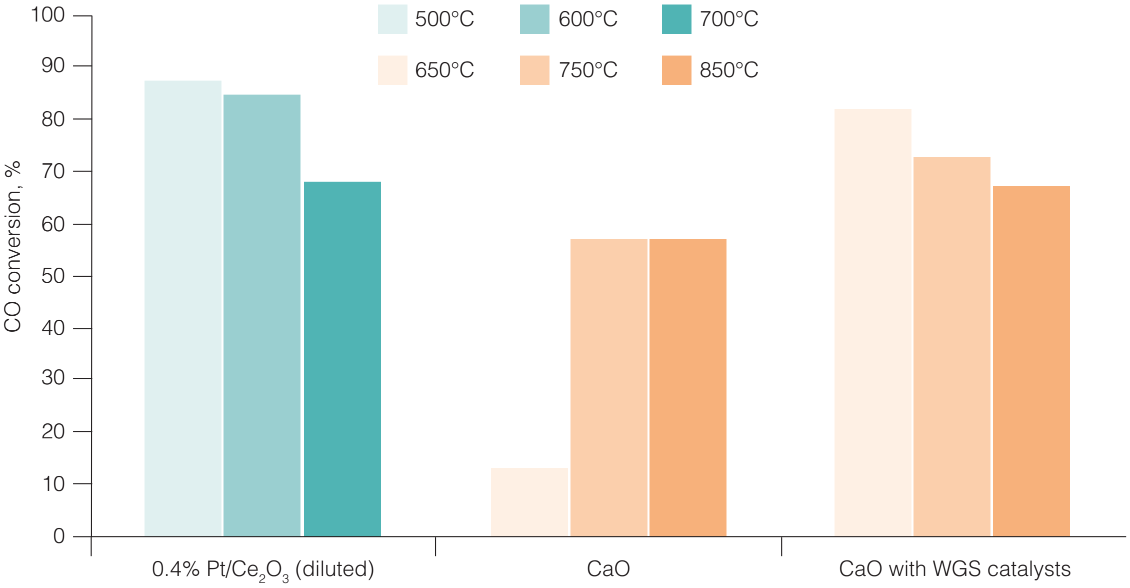


Figure 5 CO conversion over CaO with and without WGS catalyst (Shamsi, 2008)

tested during the WGS reaction at 400°C and 1 MPa in the presence of a Pt/Ce_2O_3 catalyst. The 10:1 CaO:NaOH sorbent possessed the highest CO_2 capture capacity of those studied, with a capacity of 10.5 mol CO_2/kg sorbent (46.2 wt%), which approaches the theoretical limit for CaO of 17.9 mol CO_2/kg (78.8 wt%). It was also found that the sodium-promoted sorbent regenerates at a lower temperature.

A patented precipitated calcium carbonate (P.C.) sorbent has been studied by Ramkumar and others (2008, 2011). The morphological properties of the PCC sorbent can be tailored using surface modifiers to form a mesoporous structure that results in superior performance over naturally occurring limestone and dolomite sorbents. The PCC sorbent demonstrated a high CO_2 capture capacity of about 70% by weight while removing H_2S impurities at high temperatures to ppm levels and producing high purity hydrogen at elevated pressures in the absence of a catalyst. Life cycle testing of the sorbent over multiple cycles of carbonation-calcination reactions showed that the PCC sorbent attains a capture capacity of 40–36 wt% over 50–100 cycles, which is significantly higher than most of the high temperature sorbents reported in literature. The purity of hydrogen produced was increased by a large extent when the carbonation reaction was integrated with the WGS reactor. The steam addition for the WGS reactor could also be reduced to stoichiometric quantities which aids in reducing the parasitic energy consumption of the process. In addition, the extent of H_2S removal by the CaO sorbent is also enhanced by operating at lower steam partial pressures. High purity hydrogen of 99.7% with less than 1 ppm sulphur impurity was obtained in a bench-scale fixed bed reactor system.

The feasibility and optimum process conditions for the production of H_2 in the absence of a WGS catalyst were also investigated by Ramkumar and Fan (2010a). Pressure was found to have a large effect on H_2 purity. At high pressures, typical of commercial deployment, the absence of the catalyst and the reduction of excess steam addition did not have any effect on CO conversion and high H_2 purity (>99%) was obtained at near-stoichiometric steam to carbon ratios. A greater enhancement in H_2 purity was found to occur at temperatures of 600–650°C, and the effect of CaO sorbent was found to diminish with increasing temperature. The purity of H_2 in the product stream was found to decrease with sorbent cycling from near 100% to 97% at the end of ten reaction and regeneration cycles. Also, for each additional cycle, the pre-breakthrough region was shorter than the previous one.

A three-stage ‘calcium looping’ process was studied by Ramkumar and Fan (2010b). The three reactors comprise a carbonation reactor, where the thermodynamic constraint of the WGS reaction is overcome by the constant removal of the carbon dioxide product and high purity hydrogen is produced with contaminant removal; the calciner, where the calcium sorbent is regenerated and a sequestration-ready carbon dioxide stream is produced; and the hydrator, where the calcined sorbent is reactivated to improve its recyclability. Although calcination of the sorbent under realistic conditions causes severe sintering and a loss in reactivity, sorbent reactivation by hydration was effective in restoring sorbent reactivity. In the presence of a mixture of steam and CO_2 at 900°C, almost complete calcination of the sorbent was obtained in every case. It was found that, upon calcination of the limestone sorbent in an atmosphere of 33% steam and 67% CO_2, a CaO sorbent with a CO_2 capture of 35 wt% was obtained. A further increase in the steam concentration to 50% resulted in the production of a more reactive sorbent with a CO_2 capture of 45 wt%.

Detailed thermodynamic analyses of different gasifier systems showed that an operating temperature window of 500–750°C is suitable for the production of pure H_2, for steam to carbon ratios of 1:1 to 3:1 (Ramkumar and others, 2011). However, operating at near-stoichiometric steam conditions is advantageous for simultaneous sulphur removal to low levels in the product H_2 stream. Bench-scale experimental data confirmed that, for near-stoichiometric conditions, high CO conversion and H_2 purity can be obtained at high pressures and an optimal temperature of 600°C.

A concept called Thermal Swing Sorption Enhanced Reaction (TSSER) process was designed to capture hydrogen in the WGS reactor using chemisorbents (K B Lee and others, 2006, 2008). Two potential chemisorbents were identified: K_2CO_3 promoted hydrotalcite and Na_2O promoted alumina.

Simulations were carried out that demonstrated ‘remarkable’ process intensifications caused by the sorption enhanced reaction concept using the CO_2 chemisorbent. The concept allows direct production of a high purity H_2 product from a WGS reactor by simultaneously carrying out reaction and separation in a single unit operation. It was noted that the simulated observations, however, needed to be experimentally demonstrated.

Five hydrotalcite-based dry regenerable CO_2 sorbents and four CuO based WGS catalysts were prepared by spray drying techniques by J B Lee and others (2009). Their physical properties and reactivities were tested to evaluate their applicability to a fluidised bed SEWGS process for pre-combustion CO_2 capture. All the CO_2 sorbents appeared to satisfy the basic physical requirements for fluidised bed application. However, their CO_2 sorption capacity needs to improve. The CO_2 sorption capacities at ambient conditions was in the range 2.5–7.0 wt%, whereas, at pressurised conditions they were 5.0–6.8 wt%. Similarly, nine MgO based dry regenerable CO_2 sorbents and seven CuO-based water gas shift catalysts were prepared by spray drying techniques by J B Lee and others (2010, 2011) and then tested. All the CO_2 sorbents appeared to satisfy the basic physical requirements for fluidised bed application. The CO_2 sorption capacity of one of the tested sorbents was approximately 17.6 wt% at 200°C and 2.1 MPa with synthesis gas conditions. Again, it was concluded that their CO_2 sorption capacity needs to improve.

Walspurger and others (2008) point out that potassium carbonate promoted hydrotalcite-based and alumina-based materials are cheap and excellent materials for high temperature (300–500°C) adsorption of CO_2 and particularly promising in the SEWGS reaction in which multiple reactor vessels are packed with mixtures of CO_2 absorption pellets and WGS catalyst pellets. Alkaline promotion significantly improves CO_2 reversible sorption capacity at 300–500°C for both materials. However, the true nature of the species responsible for CO_2 reversible adsorption at such temperatures is still not well understood. Their experimental results showed that potassium ions strongly interact with aluminium oxide centres in hydrotalcite, generating basic sites that reversibly adsorb CO_2 at 400°C. Raman and infrared spectroscopy studies carried out by Keturakis and others (2011) have revealed the formation of surface bidentate carbonate species.

The performance of potassium promoted hydrotalcite under SEWGS conditions was investigated by van Selow and others (2009a). It was found to take up CO_2 reversibly at temperatures near 400°C with breakthrough capacities of 1.3–1.4 mmol/g (5.7–6.2 wt%) under realistic conditions. Total capacities could exceed 10 mmol/g (44 wt%) if feed partial pressures were sufficiently high (van Selow and others, 2009b). The stability of the sorbent material was shown for more than 4000 cycles of adsorption and desorption. After 1400 cycles the sorbent showed a stable cyclic stability of 0.66 mmol/g (2.9 wt%). Proof-of-principle experiments were carried out in 6 m tall reactors. When fed with a simulated syngas, it was demonstrated that CO conversion increased from 55% in the absence of a sorbent to 100% in its presence.

Magnesium carbonate formation was identified by in situ X-ray diffraction (XRD) as an important process taking place during the CO_2 adsorption step (Walspurger and others, 2010). Magnesium carbonate is reversibly formed from decomposed hydrotalcite-based material at 350°C in the presence of sufficient concentrations of CO_2 and steam. Under these conditions the total CO_2 capacity of an 11 wt% K_2CO_3 promoted hydrotalcite-based material with an Mg/Al ratio of 2.9 could reach up to 15.1 mmol/g (66.4 wt%). The presence of high pressure steam favours carbonation compared to the dehydration process leading to MgO periclase that is usually observed as result of hydrotalcite decomposition under ambient conditions and in the presence of dry CO_2. The experiments demonstrated that it is possible to reform the magnesium carbonate phase after decomposition under a dry atmosphere by using a relatively high partial pressure of steam and CO_2. Despite this, most of the extra CO_2 capacity that is induced by magnesium carbonate formation after long adsorption times was, however, not very beneficial for the SEWGS process due to the highly dynamic nature of pressure swing cycles compared to the magnesium carbonate formation and decomposition (Walspurger and others, 2011). The kinetics of the chemisorption are too slow to exploit in a pressure swing absorption process.

A new sorbent material for the SEWGS process has been developed by van Selow and others (2011). The sorbent is K-MG30, a potassium carbonate promoted hydrotalcite-based material with 30 wt% Mg, much lower than in the reference material previously used by van Selow and others (2009a,b). Pellets of the material have been tested under realistic process conditions in an experimental rig of 2 m length. The cyclic capacity of the material is 27% higher than the cyclic capacity of the reference sorbent. Moreover, 36% less steam is required for its regeneration. The sorbent pellets also have a 65% higher crush strength than the reference sorbent. In contrast to the reference material, the new sorbent does not form notable amounts of $MgCO_3$ under the relevant operating conditions. Due to the absence of this slow CO_2 uptake process, the sorbent remains mechanically stable, the cyclic steady state is reached rapidly, CO_2 slip in the product gas is reduced, and steam requirements are lowered. It was demonstrated that the sorbent remains mechanically stable during operation of at least 1200 adsorption/desorption cycles. With this new, higher density material, carbon capture levels exceeding 95% can be obtained more efficiently and vessels will be smaller.

The sorption enhanced WGS technology is attractive for pre-combustion decarbonisation of power production based on IGCC, but only when the SEWGS technology can be applied for sour syngas according to van Dijk and others (2011a). To this extent, they demonstrated that 2000 ppm of H_2S did not influence the CO_2 sorption behaviour of a potassium promoted hydrotalcite material at a relatively low pressure of 0.5 MPa. They tested the sorbent at PSA conditions between 3 MPa adsorption and 0.2 MPa regeneration. The sorbent has good catalytic activity for the WGS reaction under SEWGS conditions. Although the sorbent's steady-state WGS activity is 2 to 4 orders of magnitude lower than observed for commercial FeCr based and CoMo based catalysts, the H_2 product of the sour SEWGS process is essentially free of CO, CO_2 and H_2S at 3 MPa pressure and 400°C feed temperature when feeding a syngas containing 200 ppm H_2S. Prior to CO_2 saturation of the sorbent, full CO conversion and simultaneous capture of the produced CO_2 was observed. At the moment the sorbent starts to get saturated with CO_2, the WGS activity drops as evidenced by the slightly earlier breakthrough of CO compared to CO_2. Following breakthrough, the sorbent WGS activity is significantly lower. Since mainly pre-breakthrough WGS activity is relevant for SEWGS operation aiming at high CO_2 capture ratios, these results suggest that a supplementary WGS catalyst material is not required. It was also demonstrated that the presence of 500 ppm H_2S in the syngas did not appear to influence the CO_2 sorption characteristics. H_2S did not appear to change the CO_2 sorption capacity of the sorbent materials studied. Later, the suitability of the sorbent was demonstrated by means of adsorption and regeneration experiments in the presence of 2000 ppm H_2S (van Dijk and others, 2011a,b). In multiple cycle experiments at 400°C and 0.5 MPa, the sorbent displayed reversible co-adsorption of CO_2 and H_2S. Again, the CO_2 sorption capacity was not significantly affected compared with sulphur-free conditions.

A search for new SEWGS sorbents by using high throughput techniques was reported by Bakken and others (2011). The aim was to find sorbents that were more efficient than potassium promoted hydrotalcite. In total 432 new sorbent formulations were prepared, partly characterised and more than 300 sorbents were evaluated under realistic conditions in a three cycle adsorption-desorption test. The sorbents were prepared by stepwise impregnation of water solutions of various metal nitrates (typically 2–5) onto porous γ-alumina or silica spheres. The sorbents were calcined at 500°C before performance evaluation. From the evaluation, four leads have been selected for upscaling and testing for sorption performance and particle stability under SEWGS conditions.

4.11 Comments

Simultaneous CO_2 and H_2S capture in a SEWGS environment looks promising but the H_2S would have to be removed from the CO_2 prior to storage. It is not yet clear how separate H_2S and CO_2 streams could be produced if they have been captured together. Also, it is not clear how much make-up sorbent would be needed in the SEWGS. It would probably be less than that needed if the sorbent is located in the gasifier but it could possibly be of the same order. If there are large quantities of sorbent to be disposed of, then integration with cement production would probably be necessary but this could limit IGCC plants with SEWGS CO_2 capture to locations close to cement production.

However, there is still no commercially available adsorption process for pre-combustion capture (Ciferno and others, 2011). They have also pointed out that:

> *The closest application of an adsorption process for CO_2 separation is the PSA process for H_2 purification from syngas. However, H_2 purification is different from a CO_2 removal process. In H_2 purification, the purity of H_2 is the key parameter, whereas the recovery of H_2 is not as critical. For an IGCC power plant with CO_2 capture, H_2 recovery rate and CO_2 purity are both important, but the H_2 purity (above 93 per cent) and CO_2 recovery rate (above 90 per cent) can be compromised. As a result, an H_2 purification process designed to produce highly pure H_2 would require modification to facilitate the new requirement of CO_2 capture and sequestration.*

5 Membranes

The use of membranes in post-combustion carbon dioxide capture has been discussed in an IEA CCC report by Davidson (2009). However, membrane removal of CO_2 from flue gas is difficult due to low driving force and the presence of trace contaminants which are molecularly very similar to CO_2, such as SO_2. Separation of CO_2 from fuel gas is more advantageous since it is already at high pressure and possesses a higher concentration of CO_2 after the WGS (Luebke and others, 2005). Pennline and others (2006) have pointed out that simplicity, flexibility, the ability to maintain high CO_2 pressure, and the potential to perform separations at low energy penalties make membranes interesting for CO_2 removal for IGCC applications. In addition to the standard requirement of obtaining high permeability, challenges exist in the development of membranes capable of selectively separating CO_2 from the process gas stream. In addition, the reducing conditions and the presence of water and various minor contaminants necessitate the design of membranes with exceptional chemical and physical stability. However, if a membrane can be fabricated to withstand higher temperatures (150–370°C), an additional benefit with respect to maintaining the higher thermal efficiency of the plant (as compared to cold scrubbing of CO_2) could be obtained (Pennline and others, 2008). The use of membranes for carbon capture in gasification systems was reviewed by Li and Fan (2008) and more recently, very thoroughly, by Scholes and others (2010). A detailed overview of existing concepts for the use of membranes for pre-combustion capture of CO_2 in IGCC has also been produced by Scherer and Franz (2011).

Membranes can either be CO_2 or hydrogen selective; Carbo and others (2006) compared two advanced membrane reactor configurations for use in an IGCC with carbon capture. The configurations had a WGS reactor for synthesis gas conversion, which was integrated with a hydrogen- or carbon dioxide-selective membrane reactor. They used exergy analysis to optimise each of the energy conversion systems. Preliminary results indicated that IGCC with CO_2 capture through CO_2-selective WGS membrane reactor has one important disadvantage compared with the H_2-selective system, namely the elevated efficiency penalty. However, advantages of the CO_2-selective membrane reactor include the resulting CO_2 purity and the flexibility with respect to fuel conversion and CO_2 separation. The disadvantages are that the H_2 product in the retentate will contain a certain amount of CO_2 and the CO_2 product in the permeate will be at a lower pressure and has to be compressed further. Much of the research on hydrogen-selective membranes has been directed at producing a pure hydrogen product rather than capturing carbon dioxide. The advantages of an H_2 selective membrane are that CO_2 product in the retentate will be at high pressure (less compression work is required) and pure H_2 in the permeate can be easily achieved. The disadvantages are that it is difficult to achieve a high H_2 recovery rate (some H_2 will remain in retentate) and the CO_2 product in the retentate has to be further purified. Generally speaking, a membrane process has difficulty to achieve both high recovery rate and high purity of the same product in one stage (Ciferno and others, 2011).

Scholes and others (2010) point out that, in general, CO_2 selective membranes for an IGCC process are significantly less advanced than H_2 selective membranes, and considerably more research is required before they can be applied to the process. Also, in contrast to H_2 production systems where the high H_2/CO_2 selectivity favours ultra-high selectivity membranes, the requirements for IGCC indicate that a wider range of materials, including ceramic and zeolite-based membranes, should be considered (Ku and others, 2011).

It may not be an either/or choice of membrane; simulation carried out by Doong and Jadhav (2006) showed that a complementary membrane reactor incorporating both CO_2-selective and H_2-selective membranes offered the highest hydrogen production, the highest CO_2 production and the lowest retentate flow than the process employing only H_2-selective or CO_2-selective membrane reactor. The CO conversion of the shift reaction was increased by the synergetic effect of the two complementary membranes in a single reactor.

Composite membranes are membranes with two or more distinct layers and the fundamental science of their use for the transport of hydrogen has been reviewed by Mundschau (2009). Issues concerning their process integration and scale-up for H_2 production and CO_2 have been addressed by Anderson and others (2009) who note that a key advantage of membranes over conventional systems is the ability to retain both hydrogen and carbon dioxide at high pressures.

5.1 Polymer membranes

Novel polymeric-metallic composite membranes for CO_2 separation at elevated temperature have been investigated by Berchtold (2005) who noted that despite the demand for membranes that can operate at high temperatures, existing membrane materials have limiting temperatures, selectivity, productivity, chemical resistance, and material properties. The aim of her work was to produce a high temperature membrane and module capable of operation at temperatures significantly higher than 150°C since commercially available membranes are limited to operating below that temperature. The polymer was based on polybenzimidazole (PBI) which is thermally stable with a glass transition temperature (T_g) of ~450°C. This was modified in various ways to improve such properties as membrane selectivity, productivity, processability, and chemical resistivity. A specially designed porous metal substrate was used to provide mechanical support for the polymer film. An operating temperature of 400°C was achieved. Later tests (Berchtold and others, 2006) revealed that the H_2/CO_2 selectivity decreases with increasing temperature. However, selectivity was still better than the state-of-the-art while operating at industrially attractive conditions. The membrane remained thermally stable for more than 330 days in operation at 250°C. Successful testing of the polymer based membrane in simulated syngas environments containing H_2, CO_2, CH_4, N_2, CO, H_2O, and H_2S from 25°C to 400°C has been reported by Ciferno and others (2011).

Krishnan and others (2009), are developing a process that is based on PBI membrane to achieve a capture of 90% CO_2 as a high pressure stream with about 10% increase in the cost of energy. A significant advantage of the PBI membrane compared with other sorbent based technologies and conventional polymeric membranes is that PBI membrane is capable of operating at over a broad temperature range (~100–400°C). Hollow fibres based on a selective layer of PBI onto a porous substrate have been produced by O'Brien and others (2009). It has been demonstrated that this selective layer can be placed on either the outside (shell side) or inside (lumen side) of the fibre. An H_2 permeability of >100 gas permeation units (GPU; $>7.5 \times 10^{-14}$ m.s^{-1}.Pa^{-1}) with an H_2/CO_2 selectivity of 40 at 250°C has been achieved (Ciferno and others, 2011). The PBI membrane also has a high permeability for steam.

The application of a highly selective fixed site carrier (FSC) polyvinyl amine (PVAm) membrane to capture CO_2 has been investigated for four different power plant scenarios by Grainger and others (2007). Two of the scenarios were for IGCC plants; one for capture from the flue gas and the other in an integrated process with CO shift. Simulations revealed that the partial pressure of the CO_2 in the target stream was critical to the performance of the membrane separation. The flue gas option with a CO_2 partial pressure of 9 kPa required feed compression, sweep and vacuum on the permeate to achieve greater than 60 vol% purity of the recovered CO_2. Membrane area requirements were large (19 m^2/kg of CO_2 recovered/h). The integrated scenario, however, with a partial pressure of 0.82 MPa, achieved purity greater than 90 vol% at 80% recovery and with energy requirements lower than that for typical amine absorption. The membrane area was calculated to be 2 m^2/kg of CO_2 recovered/h.

Grainger and Hägg (2008) list the benefits of using FSC membranes:
- lower energy consumption than in a solvent unit;
- no solvent make-up or chemical inventory required;
- a smaller footprint.

The commercial multi-block copolymers Pebax (poly(amide-b-ethylene oxide)) and Polyactive (poly(ethylene oxide)-poly(butylene terephthalate)) were identified as starting materials based upon their high selectivity for CO_2 due to the high solubility of this gas within the polymers by Czyperek and others (2010). Systematically adding polyethylene glycol ethers to Pebax and Polyactive led to an impressive enhancement in CO_2 permeability and CO_2/H_2 selectivity. With Pebax/polyethylene glycol membranes, mixed CO_2/H_2 selectivities of around 9 were obtained.

However, there is still much scope for improving the selectivity of polymer membranes. An evaluation of H_2 and CO_2 selective membranes showed that, with state-of-the-art membranes (CO_2/H_2 selectivity 15.5, H_2/CO_2 selectivity 5.91), the current requirements concerning CO_2 purity and CO_2 separation degree cannot be fulfilled (Franz and Scherer, 2010; Czyperek and others, 2010).

The CO2CRC/HRL Mulgrave membrane pilot plant was designed to separate 5.6 $kgCO_2$ per day from H_2 and N_2 in syngas. The small scale of the plant allowed a range of membrane materials and membrane separation strategies to be trialled for separating CO_2. The pilot plant includes a pre treatment section where the syngas is cooled to atmospheric temperature to remove condensables and then reheated to at least 35°C. Results using a polysulphone base membrane operating at 35°C have been reported by Anderson and others (2011). It was found that the membrane was unable to purify carbon dioxide to the concentration required, and therefore additional multi-stage membrane separation was needed. Other membrane types tested have proved more effective, with a maximum CO_2/H_2 selectivity of 7.4 and CO_2/N_2 selectivity of 25.7 recorded for a rubbery polymeric membrane at 50°C. The principal lesson from the membrane operation was an understanding of the impact of minor components within the syngas upon performance. Liquid hydrocarbons and coal dust have had less of an impact on the membrane unit than on the solvent operation (*see* Section 3.2), possibly due to the use of a pre-treatment operation which removed the majority of these components. Conversely, performance deterioration through exposure to high water partial pressures was often observed . The impact of water, in combination with elevated operating temperatures proved to be the most challenging problem.

More details on the effects of the minor components have been reported by Scholes and others (2011) for polymeric Matrimid 5218 membranes. Matrimid 5218 is a soluble thermoplastic polyimide based on a proprietary diamine, 5(6)-amino-1-(4′ aminophenyl)-1,3,-trimethylindane. Asymmetric flat sheet Matrimid 5218 membranes were tested on industrial unshifted syngas, as part of the CO2CRC Mulgrave capture project. For this multi-gas application, minor components such as H_2S, water and hydrocarbons, in addition to the significant quantities of CO, N_2 and H_2, all serve to reduce CO_2 permeance. However, partly as a consequence of this competitive sorption, the membrane displayed relatively good H_2 permeance and selectivity in the mixed gas environment. Under unshifted syngas conditions the membrane does not produce a CO_2 rich permeate. Rather the membrane acts to increase hydrogen concentrations. Specifically, the membrane reduces the amount of N_2, CO and CH_4 in the permeate gas compared with the syngas. Such a membrane separation might be used upstream of a solvent absorption process, which could be significantly smaller and hence more cost effective than if used alone, or it could be incorporated into a membrane reactor arrangement to enhance the WGS reaction by removing product hydrogen as it forms.

Membrane Technology and Research Inc is developing a new polymer membrane and membrane separation process to capture carbon dioxide from shifted synthesis gas generated by a coal-fired IGCC power plant (Ciferno and others, 2011). The goal is to prepare composite polymer membranes and bench-scale modules that have H_2/CO_2 selectivities of 10 or higher and hydrogen permeances of greater than 200 GPU (15×10^{-14} $m.s^{-1}.Pa^{-1}$) at syngas clean-up temperatures of 100–200°C. The (unidentified) membranes have shown stable performance treating syngas containing up to 780 ppm hydrogen sulphide. The average membrane performance (H_2/CO_2 selectivity of 15–25 and H_2 permeance of 200–300 GPU or 15–22.5 × 10^{-14} $m.s^{-1}.Pa^{-1}$) has exceeded project targets.

The University of Texas at Dallas is preparing novel, non-precious metal mixed-matrix membranes (MMMs) in flat, tubular, and hollow fibre geometries based on polymer composites with nanoparticles of zeolitic imidazolate frameworks (ZIFs). Membrane performance to separate hydrogen from synthesis gas generated during coal gasification will be evaluated in an integrated WGS membrane reactor. The goal is to exploit the high surface areas, adsorption capacities, and sieving capabilities of the nanoporous ZIF additives to achieve unprecedented, selective transport of hydrogen (Ciferno and others, 2011). Measurement of hydrogen sorption in thermally stable molecular sieve ZIFs showed H_2 adsorption up to 350°C and 10 MPa, while retaining the ZIF's integrity. ZIF/PBI MMMs exhibited a 130% increase in H_2 permeability with a 28% reduction in H_2/CO_2 selectivity at 35°C and 30.3 MPa.

5.2 Silica membranes

Molecular sieve silica (MSS) membranes work by passing H_2 through and blocking other gases such as CO_2 (Duke and others, 2007). Inorganic membranes derived from silica were scaled up by 20 times from small plate ceramics to tubes. Initial results from the work on development and scale-up indicated that these membranes can purify hydrogen from a gasification plant, but more work is needed to address scale-up. The work has shown that silica membranes can be successfully applied to larger geometries, achieving purity requirements.

Diniz da Costa and others (2009) investigated the proof-of-concept of metal (cobalt) doped silica membranes for H_2/CO_2 separation in single and multi-tube membrane modules, in addition to a membrane reactor configuration for the high temperature WGS reaction. A multi-tube membrane module was tested up to 300°C and 4 atmospheres for 55 days (1344 hours) for binary feed gas mixtures containing H_2 and CO_2 at 40:60 concentration ratio. The best membrane performance delivered H_2 purity in excess of 98%. For the high temperature WGS reaction and a ternary mixture of 40% H_2, 40% CO_2 and 20% CO, which is equivalent to 67.5% CO conversion, the membrane delivered a permeate stream containing 92.5% H_2 about 5.5% lower than the results obtained for a binary mixture. These results strongly suggest that the separation of a ternary gas mixture is more complex than a binary mixture. The purity of H_2 in the permeate stream increased from 60% to 92.5% as the temperature increased from 300°C to 375°C, respectively. In turn, this effect was combined with high CO conversion for the WGS reaction, thus allowing for high throughput of H_2 production and separation in a single processing step.

5.3 Ceramic membranes

Ceramic microporous membranes that operate at intermediate temperatures ($\leqslant$400°C) for H_2/CO_2 separation have been developed by Czyperek and others (2010). Sol-gel manufactured oxides and oxide mixtures of ZrO_2/TiO_2 were prepared for both CO_2/N_2 and H_2/CO_2 separation. The first stability tests of different ZrO_2/TiO_2 compositions indicated a higher stability for ZrO_2-rich compositions. However, further optimisation of sol-gel recipes and coating procedures is necessary to develop sol-gel derived membranes with molecular sieving properties. Structurally microporous zeolites were also synthesised and tested for H_2 separation. Two types of zeolites exhibiting high stability were identified. Again, additional work is required to improve the fabrication methods of the supported membranes and their selectivity.

Perovskites have been considered as hydrogen selective membranes. They are metal oxides of the general formula ABO_3 where A is a divalent cation such as calcium, magnesium, barium, or strontium and B is trivalent such as cerium or zirconium. However, Elangovan and others (2009) have pointed out that the thermochemical stability of perovskite membranes in a syngas environment is a major hurdle that needs to be overcome. They developed a ceramic-ceramic composite material in which both the hydrogen ions and electrons generated by the dissociation of the H_2 molecule migrate independently. The composite material was produced by mixing a perovskite with doped ceria (CeO_2). Initial results using a 35 µm thick membrane showed 'exceptional' stability in a high pressure syngas environment.

5.4 Silated membranes

Silated membranes are prepared by the grafting of organosilanes onto an inorganic surface such as alumina. Attachment is accomplished when halogen atoms on the silane molecule interact with hydroxyl groups on the inorganic surface, eliminating HCl and forming a covalent attachment. As many as three such interactions can occur per silane molecule, anchoring it to the surface. Since the silane molecule can also contain nearly any organic group, this method provides an extremely flexible tool for surface modification. Membranes useful in CO_2 abatement for IGCC have been developed using this method by Luebke and others (2005; *also* Pennline and others, 2006). The membranes are described in more detail by Luebke and others (2006b). Commercial γ-alumina supports were modified with a variety of trichlorosilanes intended to enhance the surface adsorption of CO_2. CO_2 philic groups on the ends of the organosilanes enhance the preferential surface diffusion of the CO_2 across the membrane. The resulting hybrids were characterised using X-ray photoelectric spectroscopy and Fourier transform infrared spectroscopy and tested for performance in the separation of He and CO_2. The silanisation temperature was determined to be important because membranes fabricated at 273 K had substantially different performance properties than those fabricated at room temperature. Specifically, the permeances of membranes modified with alkyltrichlorosilanes at reduced temperatures were 1–2 orders of magnitude higher than those of membranes fabricated at room temperature. Despite the high permeance of the membranes, none of the samples approached the selectivity deemed necessary to be competitive as a CO_2 capture technology for IGCC processes.

5.5 Metallic membranes

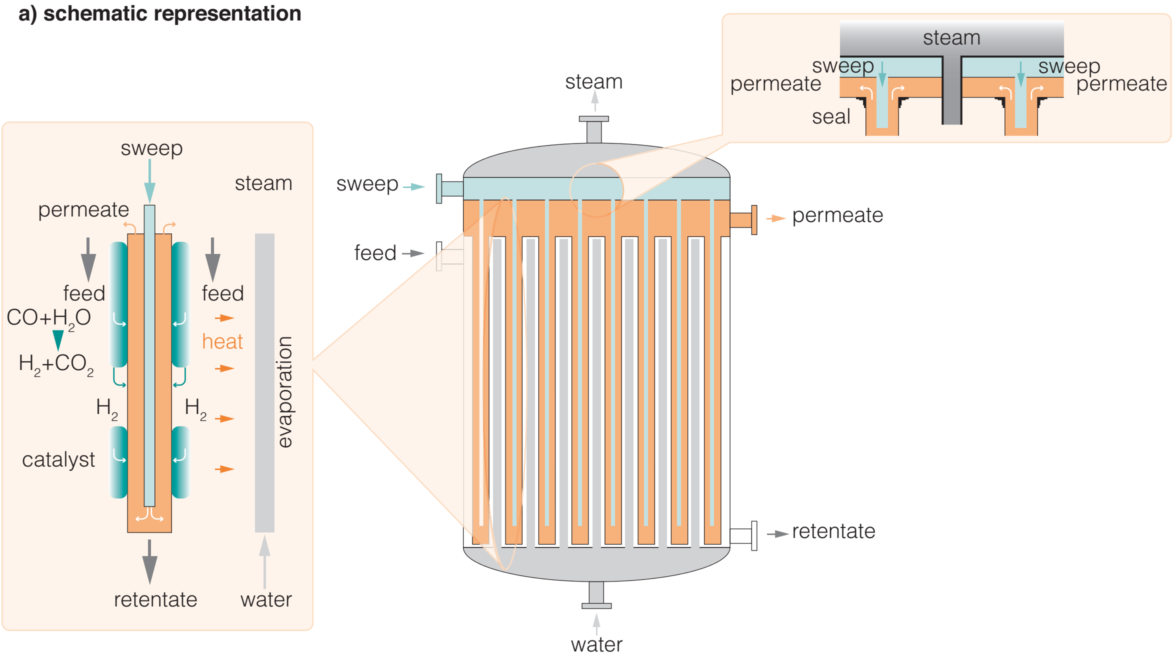
Chiesa and others (2006, 2007) proposed that a possible solution to capture the CO_2 produced by fossil fuel fired power plants before it is released to atmosphere, consisted of a modified IGCC plant incorporating a hydrogen separation membrane reactor (HSMR). They focused on supported palladium-silver (Pd-Ag) membranes with the aim of assessing the performance and estimating the cost of electricity production at virtually zero CO_2 emissions from a coal-fired IGCC plant incorporating an HSMR. Pd-Ag membranes allow the selective migration of hydrogen to the permeate side. The HSMR is positioned downstream of an adiabatic WGS reactor in order to shield the relatively delicate and expensive HSMR from severe thermal stress and to increase the catalyst life. The feed side of the reactor contains a catalyst so that, thanks to the continuous permeation of H_2 through the membrane walls, the WGS reaction advances, further improving the conversion to CO_2 and H_2. The HSMR is arranged in the shell and tubes configuration as shown in Figure 6. The feed stream flows from top to bottom on the shell side filled with WGS catalyst. Hydrogen permeates through the tubular membranes and is collected by the sweep gas, delivered by means of concentric inner tubes. Hydrogen separation relies on the capability of a dense layer of Pd-Ag alloy to activate a transport mechanism based on the following stages:

1 dissociative adsorption of hydrogen on the feed side of the membrane surface;
2 diffusion of protons through the metal lattice;
3 proton recombination to hydrogen molecules on the permeate side surface;
4 desorption of molecular H_2.

The consequences of such a mechanism are that, excluding leakages, H_2 selectivity is infinite (that is, H_2 is separated at 100% purity) but, since sulphur prevents catalytic dissociation of H_2 molecules, H_2S concentration in the cleaned syngas must be kept below 20 ppm in order to prevent poisoning and failure of the catalytic properties of Pd. Unalloyed palladium and palladium-silver alloys are highly susceptible to poisoning by H_2S. Parts per billion by volume of H_2S are sufficient to convert palladium in unalloyed membranes as well as in Pd-Ag membranes into bulk Pd_4S, which irreversibly damages membranes. This is distinct from simple poisoning of membranes by adsorption of sulphur, which is reversible (Jack and others, 2007).

Calculations by Chiesa and others (2007) indicated that, when 85 vol% of the H_2+CO in the original

a) schematic representation



b) HSMR shell-and-tube arrangement

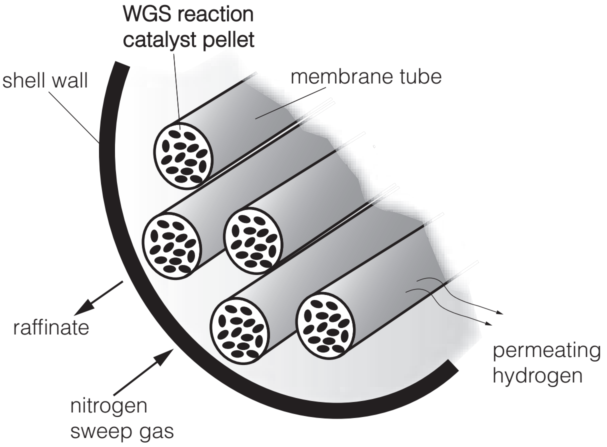


Figure 6 **WGS reactor** (Chiesa and others, 2006, 2007)

syngas is extracted as H_2 by the membrane reactor the membrane-based IGCC systems are more efficient by ~1.7 percentage points than the reference IGCC with CO_2 capture based on commercially ready technology.

Chiesa and others (2007) admit that, despite many small-scale experiments with membrane reactors, the HSMR they envisioned is presently just an abstraction. The real device would be very large (with almost a football field of surface area, ~34,000 m^2), expensive and probably relatively delicate. It remains to be demonstrated that such a unit can withstand attack by a chemically aggressive (and, compositionally, quite variable) coal synthesis gas at high temperature and pressure over the life of the plant. Further, substantial capital cost savings do not appear achievable by means of HSMR technology considering that palladium, an expensive material, is required for the membrane reactor.

Jack and others (2007) point out that metallic dense membranes, such as those based upon palladium, are essentially 100% selective for hydrogen, transporting dissociated hydrogen through atomic interstitial sites, which block even the transport of helium. Dense membranes can purify hydrogen to the highest degrees. However, some carbon and oxygen atoms can diffuse along dislocations and react with hydrogen to form CH_4 and H_2O, causing minor contamination of the hydrogen permeate. Dense membranes, whether they be palladium based, or based upon metals such as niobium, tantalum, titanium, vanadium or zirconium, transport hydrogen in a dissociated form, that is, as protons, H^+, as hydride, H^-, or as neutral atoms, H^0. This implies that membranes must have catalytic activity for the adsorption and dissociation of molecular hydrogen on the retentate (or feed) side surface and catalytic activity for the recombination and desorption of hydrogen on the permeate (or sweep) side surface. It is also pointed out that protecting membrane catalysts from the various potential catalyst poisons originating from coal (S, P, Cl, Br, As, Bi, Sb, Pb, Hg, Se, etc) is a major challenge in the development of dense hydrogen transport membrane systems. Partial gas clean-up upstream from dense membranes will be critical for their function. However, by operating membranes under higher hydrogen and steam conditions and higher temperatures, membrane catalyst poisoning can be reduced relative to catalysts used for synthetic fuel production.

Klette and others (2006) reported that SINTEF had developed a method of producing Pd membranes based on a two-step process where a defect free membrane is first prepared by sputtering deposition onto a support with a high surface finish. In a second step the membrane is transferred to a porous stainless steel support. In this way the membrane preparation can be carried out without the influence of the porous support. This allows the preparation of very thin (~1 µm) defect free membranes supported on macroporous substrates. A Pd-Ag23% tubular supported membrane was successfully tested under WGS conditions for a long time at high pressure differences and temperatures, up to 2.5 MPa and 400ºC, respectively. During a three-week test, the membrane was subjected to WGS conditions for four days. The H_2 permeance during WGS conditions was found to be 8.1×10^{-7} mol·m^2·s^{-1}·Pa^{-1}. It was found that CO and CO_2 have a significant negative influence on the H_2 permeance at the given temperature and pressure; the thinness of the membrane was identified as the probable cause. Investigations with SEM showed that there were no obvious defects on the membrane surface and secondly, no evidence of coke formation was obtained using EDS.

Pd and Ag-Pd composite membranes formed by a thin metal layer deposited by electroless plating on commercial alumina porous tubes were prepared by Broglia and others (2007). The membranes were characterised by SEM/EDS analysis and their permeation to H_2, He and CO_2 up to 380°C was determined in a laboratory pilot loop. Membranes were integrated into a membrane reactor and low temperature WGS tests were performed with a gas mixture simulating synthesis gas composition. Preliminary results indicated that CO conversion well exceeded the thermodynamic equilibrium, and a hydrogen stream with a purity exceeding 95% was produced. The selectivity values of hydrogen versus CO_2 and He at 310°C was determined to be about 300 and 800, thus indicating that a dense layer had been obtained. Membrane selectivity at higher temperatures, however, was strongly decreased by gas leaks through the end seals at the metal/ceramic interface that limited the purity of the separated hydrogen stream. It was noted that, for membranes on ceramic supports, the development of leak-tight seals is still an open issue which could limit the adoption of the technology on an industrial scale.

An obvious disadvantage of palladium-based membranes is the high cost of palladium; this has spurred research into development of other metallic membranes. Fokema and others (2007) have provided a brief account of the development of membranes based on tantalum and nickel. The permeability of the Ta based membrane was three times greater than that of pure Pd. The durability and stability of the Ta based membrane in a moist environment was investigated. No decrease in the dry gas permeability of the membrane was observed over the course of 150 hours. The hydrogen permeability decreased 22% in the presence of 33% H_2O, but completely recovered upon removal of steam from the test stream. Hydrogen permeability approaching that of Pd was observed for a Ni based membrane and the effects of steam were similar to that observed for the Ta membrane.

Mundschau and others (2005) studied a composite membrane, 250 µm thick, fabricated using Group 4 and 5 elements (such as Nb, Ta, V, Zr). The membrane was tested under ideal hydrogen/helium conditions in the feed to demonstrate membrane capabilities in the absence of impurities derived from coal. Helium was used to check for membrane leaks. Experiments showed that the membrane was 100% selective to hydrogen, with no detectable leak of helium. In the presence of 59 mole% steam and a mixture containing 37 mole% steam and 17.8 mole% carbon dioxide, essentially identical hydrogen flux was obtained as under the ideal hydrogen/helium conditions, showing that steam and CO_2 do not adversely affect the membrane catalysts. Steam, at the concentrations employed, prevented accumulation of carbon on the membrane surface, which otherwise has the potential to deposit under dry conditions by the dissociation of CO. Addition of up to 0.1 MPa CO produced a decline in hydrogen flux. The drop in hydrogen flux was attributed to competitive adsorption of CO with H_2 for surface sites. The adsorption of CO partially blocks the adsorption and dissociation of molecular hydrogen on the feed side catalyst surface of the membrane. At the temperature tested (420°C), desorption of CO was sufficient to allow dissociative adsorption of H_2, and a respectable flux of hydrogen was maintained. Xie and others (2006) performed stability tests on the proprietary membranes with simulated WGS streams over eleven months and reported that:

- the membranes, in principle, will work with synthesis gas generated from any source;
- essentially 100% pure hydrogen is separated since the membrane works by transporting dissociated hydrogen across the membrane material;
- hydrogen recoveries of 90% or higher are possible;
- the membranes can be operated under high permeate pressures of pure hydrogen, and thus the costs associated with hydrogen compression can be substantially reduced;
- the membranes can be integrated with commercial high temperature WGS catalysts.

Dolan and others (2010) point out that the costs of membranes based on palladium appear prohibitive and that there are serious durability issues which make Pd membranes appear impractical. They note that membranes based on crystalline ternary vanadium based alloys have high flux, permeability eight times better than Pd, stable operation at 400–500°C (compatible with WGS), and relatively low cost.

5.6 Cermet membranes

Cermet membranes that contained mixed-conducting ceramics combined with a metallic component have been developed by Balachandran and others (2005, 2006a,b, 2007a,b, 2008; *also* Ciferno and others, 2011) for hydrogen separation. In these cermets, the metal enhanced the hydrogen flux of the ceramic phase by increasing the electronic conductivity of the cermet. They also dispersed a hydrogen transport metal, a metal with high hydrogen permeability (Pd, Pd-Ag, Pd-Cu, Nb, Zr, Ta, etc), in a thermodynamically and mechanically stable ceramic matrix such as Al_2O_3 or ZrO_2. These cermets exhibited the highest hydrogen flux. However, as noted above, the formation of palladium sulphide (Pd_4S) can seriously degrade hydrogen permeation though Pd-containing membranes. The chemical stability of the membranes was evaluated by equilibrating samples in 73% H_2/400 ppm H_2S/balance He at temperatures in the range 400–900°C. It was found that the a 200 µm thick cermet membrane was stable for up to ~1200 h at 900°C in gases containing up to ~400 ppm H_2S. Although the formation of Pd_4S seriously degrades the performance of Pd-containing cermet membranes, it does not necessarily destroy the membrane, because membranes can sometimes be regenerated after they react with H_2S. The ability to regenerate a membrane should depend on the extent of reaction and will be influenced by the H_2S concentration in the feed gas, the temperature at which the exposure occurs, and the duration of the exposure, among other factors.

A dense cermet membrane consisting of tantalum metal and yttria stabilised zirconia (YSZ) has been developed by Park and others (2011) to separate hydrogen from mixed model gases. The price of tantalum metal is considerably lower than that of Pd and tantalum has high permeability in comparison with other hydrogen permeable metals, but tantalum is unstable in most atmospheres since it can be easily reacted with oxygen, nitrogen and hydrogen. The reactivity and stability of Ta powder and the Ta/YSZ cermet membrane were investigated. The hydrogen flux through the Ta/YSZ cermet membrane increased with increasing temperature using 100% hydrogen as feed gas. The maximum hydrogen flux through a 0.5 mm thick membrane exposed to flowing pure hydrogen as feed gas was 1.2 ml/min.cm^2 at 500 C. During the permeation test, the Ta/YSZ cermet membrane deteriorated due to the formation of tantalum hydride. However this depended on the type of sealing system used since it was only observed for the brazing sealing cell system used to fix the membrane to a stainless steel ring. In the case of knife edge type sealing, no tantalum hydride was detected on the surface of Ta/YSZ cermet membrane.

5.7 Supported liquid membranes

Supported liquid membranes (SLMs) are prepared by impregnating porous substrates with a liquid transport media. Though performance results have often been encouraging, a major problem has been encountered with respect to long-term stability. Evaporation of the liquid transport medium eventually leads to incomplete filling of the substrate pores and membrane failure (Pennline and others, 2006, 2007, 2008; Luebke and others, 2006a; Ilconich and others, 2006). In a collaborative effort with the University of Notre Dame, supported liquid membranes were prepared by impregnation of commercial porous polymer films with a specific ionic liquid. Ionic liquids are a class of salts which are liquid at or slightly above room temperature. They possess a number of interesting properties including negligible vapour pressure. Because the variety of available anions and cations make the number of potential ionic liquids nearly limitless, it is possible to tailor them with high solubility selectivities, particularly for CO_2 over most other gases. Together with these properties, the stability of many ionic liquids to temperatures above 200°C has led to their examination as transport media in membranes designed to selectively remove CO_2 from fuel gas.

Membranes prepared with polysulphone supports were found to be stable to 125°C. The CO_2 permeability of the membranes increases from 744 to 1200 barrer ($\sim 5.58–9 \times 10^{-15}$ $m^2s^{-1}Pa^{-1}$) as the temperature increased from 37°C to 125°C. The CO_2/He selectivity decreased from 8.7 to 3.1 over the same temperature range. Operation of the membrane at temperatures greater than 135°C led to failure. However, it was argued that the failure was a result entirely of the choice of support, and the ionic liquid showed no change in degradation over the range of temperatures studied (Ilconich and others, 2007; Pennline and others, 2008). It was recognised that much work remains to be done. Supports stable to temperatures greater than 135°C in the presence of ionic liquids must be developed. Ilconich and others (2007) suggest that it is very probable that polymer supports stable to much higher temperatures in the presence of ionic liquids will be found on further investigation. Fabrication techniques must be found which allow the membranes to survive greater transmembrane pressures. Most importantly, the ionic liquid transport media must be improved to increase selectivity and permeability at high temperature. Once these problems have been solved, Pennline and others (2008) suggest that the improved permeability, diffusivity, and selectivity of these membranes over polymers could make them a key component in the pre-combustion separation of CO_2 within IGCC power generation schemes.

Myers and others (2008) prepared supported ionic liquid membrane with a cross-linked Nylon 66 polymeric support. Measurements were made up to 175°C without any loss of stability of the membrane. This was due to the high thermal stability of the support, mechanically stable above 300°C. However, the selectivity reached a maximum at 85°C and declined with increase in temperature. The temperature of the selectivity maximum is determined by the strength of the chemical complex formed with CO_2. Stronger complexes would yield higher temperature selectivity maxima limited only by the thermal stability of the materials involved.

5.8 WGS membrane reactors

Palladium-copper alloys are more resistant to the poisoning effects of sulphur at high temperatures (Coulter, 2007). Self-supporting Pd-Cu alloy membranes were produced with thicknesses down to 3 µm. Good hydrogen permeability rates were measured and the self-supporting membranes were free from the problems due to metallic interdiffusion in composite structures, and so should exhibit a long life at temperatures above 300°C. The importance of this increased sulphur-resistance is that membranes can be used in a way analogous to sorbent enhanced WGS in the form of WGS membrane reactors (WGSMRs).

Pd-Cu membranes integrated as a WGSMR were investigated by Morreale and others (2007). They also looked at the effects of H_2S on the alloy. In gas mixtures containing 0.1% H_2S, pure Pd membranes exhibited the most severe corrosion of the metals tested but this severe corrosion did not result in the largest decrease in performance. At lower temperatures (350°C and 450°C), the largest decrease was observed for the alloys that did not exhibit thick scale growth, such as 53 wt% Pd-Cu alloy. Pure Pd and 80 wt% Pd-Cu alloy were selected for use in the feasibility study of the high temperature WGSMR concept. WGSMR testing in the presence of S-free simulated syngas with residence times of two seconds resulted in CO conversions of approximately 99% for pure Pd membranes and 68% for 80 wt% Pd-Cu membranes, both of which were substantially greater than the 32% equilibrium conversion expected under the experimental conditions. Additionally, WGSMR testing was conducted with a simulated sour-syngas in which the H_2S concentration was maintained below the thermodynamic threshold for sulphides to form on the pure palladium and 80 wt% Pd-Cu membranes. The membranes retained their apparent permeability in the presence of the sour-syngas. However, a significant drop in CO conversion was observed which was attributed to catalytic deactivation of the membrane materials for the WGS reaction. Upon the introduction of sour-syngas having H_2S concentrations above the threshold for sulphidation, both membrane reactor materials failed within minutes. Degradation mechanisms applicable to dense metal hydrogen membranes were discussed in more detail by Morreale and others (2009). They concluded that the chemical degradation from syngas constituents and contaminants prohibits the widespread application of hydrogen membrane technologies to fossil fuel conversion processes.

Tests by Roa and others (2009) using a 7 µm thick Pd-Cu composite membrane revealed that H_2S caused a strong inhibition of the H_2 flux of the membrane which was accentuated at levels of 100 ppm or higher. Adding 5 ppm to the WGS feed gas mixture reduced the H_2 flux by about 70%, but this inhibition was reversible. The membrane was exposed to 50 ppm H_2S three times without permanent damage. Above 100 ppm, the membrane suffered some physical degradation and its performance was severely affected. A Pd-Au membrane was also tested but its H_2S tolerance was not reported. In a WGS mixture, no H_2 flux reduction was observed compared with a pure H_2 gas at the same conditions. Inhibition of the flux was observed for the Pd-Cu membrane for similar WGS experiments.

A modelling study to identify a stabilised Pd-Cu alloy with a commercially attractive permeability and sufficient thermal and chemical stability for practical application to hydrogen production from an advanced WGSMR was undertaken by Opalka and others (2007). It was predicted that a small amount of a transition metal substituted for copper on the Cu sub-lattice should meet the thermal and chemical stability goals. Further, it was predicted that this new trimetallic alloy should be sufficiently sulphur tolerant to meet the demands of an advanced WGSMR operating at 4.25 MPa on 'pre-cleaned' dry oxygen-blown bituminous coal gas at a 3.1 H_2O to C ratio.

Ozdogan and Wilcox (2010) have investigated H_2 and H_2S interactions on Pd-Nb and Pd-Cu alloy surfaces. They observed that the addition of Nb increased the H_2S affinity of the Pd surface whereas the opposite occurred with the addition of Cu. For Pd-Cu the adsorption energy for H_2 is remarkably lower than that of H_2S. This shows that Cu prefers to bind to H more than atomic S.

Pd-Cu membrane alloys with a palladium content greater than 60 atomic per cent palladium have been evaluated for hydrogen separation permeability by She and others (2011). For temperatures greater than 400°C at operating pressures up to ~1.4 MPa, it was found that the presence of gas species other than hydrogen, including H_2S at concentrations up to 39 ppmv, had a negligible effect on the measured hydrogen flux. In addition, after over 1000 hours of gas mixture testing, with more than 600 hours of exposure to H_2S, the Pd-Cu alloys showed no indication of performance degradation.

A NETL project is investigating Pd alloys (Ciferno and others, 2011). A dozen binary and ternary alloy spreads have been fabricated. Six have been exposed to high temperature syngas, representative of actual coal gas conditions. Four of the ternary spreads had shiny areas after exposure that indicate exceptional carbon and sulphur tolerance (170 ppm H_2S). Raman spectroscopy of the shiny areas showed little or no sulphides or carbon compounds present on the Pd alloy surface.

WGSMRs present a very challenging operating environment for the membrane. In addition to the sulphur tolerance, the membrane would need to be resistant to a number of other compounds, such as methanol, high molecular weight hydrocarbons, and coke (carbon deposition), produced as side-products from the catalysed WGS reaction. The membrane would also be subject to temperature gradients resulting from the exothermic heat of reaction (Marano and Ciferno, 2009).

A 2 l/min WGSMR for pre-combustion CO_2 capture has been developed by S H Lee and others (2011). The WGS reaction was carried out using two catalytic reactors and a Pd-Cu membrane reactor in order to investigate the CO conversion performance with simulated syngas. Also the change in CO_2 concentration after the Pd-Cu membrane reactor was measured. With a gas concentration of CO: 65, H_2: 30, CO_2: 5% and 1000 ml/min gas flow rate, total CO conversion in two-stage WGS reactors reached 99.5%. The gas concentration before the membrane reactor was H_2: 56.28, CO_2: 43.48, CO: 0.24%. The permeate was 100 H_2 and the gas concentration of the retentate flow was H_2: 35.74, CO_2: 63.27, CO: 0.99%. From these data, it is apparent that the Pd-Cu performs much better as a means of hydrogen production rather than of CO_2 capture.

A challenge for WGSMRs is that coke formation, a side product of the WGS reaction, and temperature gradients resulting from the heat production during the WGS reaction could lead to operational problems with membranes. The membrane would have to be sulphur tolerant and impermeable to water vapour. Otherwise, a membrane would be disadvantageous as it decreases the H_2O/CO ratio for the WGS reaction (Scherer and Franz, 2011).

5.9 Integration into IGCC plants

Gas separation membranes can be integrated into a number of different locations in the IGCC process in addition to post-WGS, the preferred location for current absorption technologies. Due to the many integration options possible, membranes could potentially be required to operate over a wide range of conditions. Marano and Ciferno (2009) have pointed out that it is preferred that the membrane operate at pressures and temperatures normally encountered at that point in the IGCC flowsheet where it is being placed. And, clearly it is beneficial that the membrane be placed in a location with relatively high pressure in order to maximise separation. If this is possible, the feed and product gases need not be compressed/expanded or heated/cooled. However, the membrane materials being considered, whether ceramic, metallic or polymeric, have physical and chemical limitations in regards to operating temperature and tolerance to various compounds that might be present in synthesis gas. It is therefore unlikely that one type of membrane will be able to perform over the entire range of conditions possible. They identified areas where membranes might be effectively integrated into the IGCC process. Based on the operating limitation for the membrane materials and the IGCC process temperature, it was possible to make some inferences with regard to membrane placement. This comparison is shown graphically in Figure 7. This figure also identifies current factors limiting the operating temperatures of the various materials. Desired operating temperature is a key factor in screening membrane materials for integration with IGCC. Given the wide range of temperatures, it was concluded that more than one type of membrane material will most likely be needed.

Possible points for membrane integration into IGCC plants are also discussed by Scherer and Franz (2011). They have noted that the membrane characteristics have to match the process conditions at the integration point. If the syngas has to be cooled/heated or compressed/expanded just to integrate the membrane systems, further efficiency losses will result.

5.10 Comments

Combining shift catalysis with membrane separation in membrane reactors could reduce the number of process stages and significantly improve process efficiencies, enable operation at higher

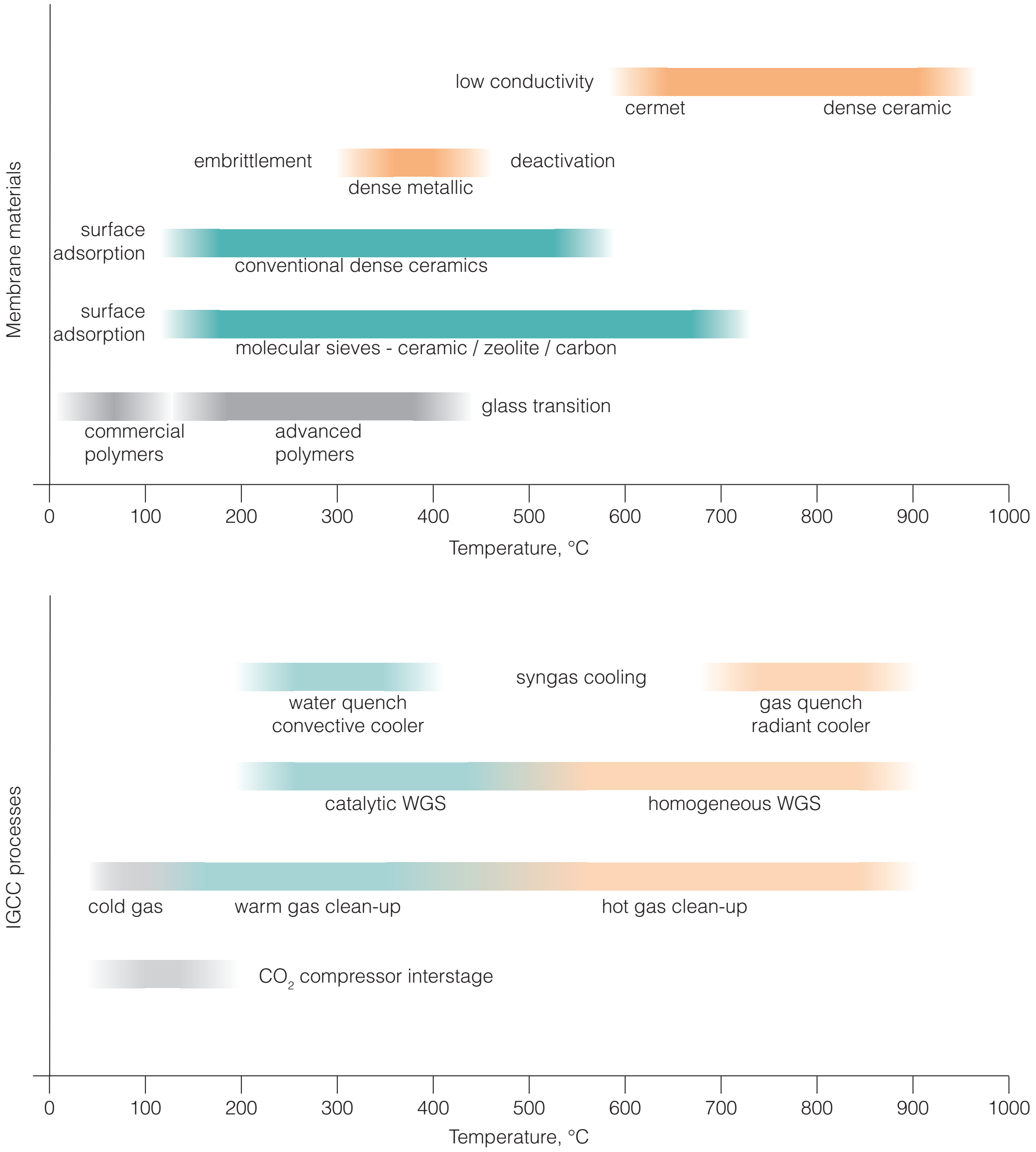


Figure 7 Temperature match for membrane/IGCC integration (Marano and Ciferno, 2009)

temperatures, and reduce steam consumption. However, there is still scope for improving the reliability and durability of membranes in a coal syngas environment.

Commercialisation of high temperature hydrogen membranes must surmount challenges of
1 manufacturing membranes with consistent high flux properties and long lifetimes:
2 fabrication of the membrane units themselves with gas inlet and outlet interconnects.

Additional research, development, and demonstration will be necessary to advance hydrogen membrane technologies to commercialisation (Plunkett and others, 2009a).

Equally, though, if CO_2 capture is the principal objective, then it is not possible to disagree with Scholes and others' (2010) conclusion that considerably more focus needs to be placed on membrane systems that have high selectivity for CO_2 over H_2.

Table 4 Technical advantages and challenges for pre-combustion membrane technologies (Ciferno and others, 2011)

Membrane type	Advantages	Challenges
H_2/CO_2 membrane	H_2 or CO_2 permeable membrane: – No steam load or chemical attrition H_2 permeable membrane only: – Can deliver CO_2 at high pressure, greatly reducing compression costs. – H_2 permeation can drive the CO shift reaction toward completion – potentially achieving the shift at lower cost/higher temperatures.	– Membrane separation of H_2 and CO_2 is more challenging than the difference in molecular weights implies. – Due to decreasing partial pressure differentials, some H_2 will be lost with the CO_2. – In H_2 selective membranes, H_2 compression is required and offsets the gains of delivering CO_2 at pressure. – In CO_2 selective membranes, CO_2 is generated at low pressure requiring compression.
Membrane/liquid solvent hybrids	– The membrane shields the amine from the contaminants in flue gas, reducing attrition and allowing higher loading differentials between lean and rich amine.	– Capital cost associated with the membrane. – Membranes may not keep out all unwanted contaminants. – Does not address CO_2 compression costs.

Dolan and others (2010) point out that the costs of membranes based on palladium appear prohibitive and that there are serious durability issues which make Pd membranes appear impractical.

Finally, a summary of the technical advantages and challenges related to pre-combustion membrane-based technologies has been prepared by Ciferno and others (2011) and is shown in Table 4.

6 Techno-economic studies

It is not the intention of this chapter to provide an authoritative techno-economic assessment of CO_2 capture in coal based IGCC power plants but, rather, simply to report the conclusions of some studies that have been made in this area where there are very few data available on which to base economic assessments. Simshauser (2005) has pointed out that the likely cost of the first IGCC plant with CO_2 capture and storage will be high, at least by comparison with existing power generation technologies. Unlikely to be economic inside the next 20 years, in order for IGCC with CCS to move down its experience cost curve, some form of explicit subsidy will be required to kick-start the development cycle.

Davison and others (2005) summarised IEA GHG assessments of the performance and costs of coal based IGCC with and without CO_2 capture. The sensitivities to a variety of potentially significant parameters were assessed, including the type of gasifier, the gasifier operating pressure, the type of CO-shift converter and co-separation of H_2S and CO_2. It was concluded that the cost of electricity (COE) from an IGCC plant with CO_2 capture was estimated to be 5.6 c/kWh for a plant based on Chevron-Texaco (now GE Energy) slurry feed gasifiers and 6.3 c/kWh for a plant based on Shell dry feed gasifiers. Capturing CO_2 increases the COE in an IGCC by 1.1–1.5 c/kWh, about 25–30%. This corresponds to 16–24 €/t of CO_2 emissions avoided, compared with IGCC plants without capture. It was suggested that improvements in IGCC technology up to 2020 were expected to reduce the COE with CO_2 capture by 20–30%, to about 4.5 c/kWh.

The US Environmental Protection Agency considers IGCC as one of the most promising technologies in reducing environmental consequences of generating electricity from coal and commissioned a report from Nexant Inc (2006). In the report, it was clearly pointed out that the economic and environmental information related to IGCC and other advanced combustion systems is changing quickly. The data and analysis presented in the report was an evaluation of information available as of February 2006. It was concluded that the then currently available carbon management technologies for IGCC were much more cost effective than similar technologies for removing CO_2 from pulverised coal (PC) plant flue gases using MEA as solvent. The major performance and economic impacts of applying these technologies to IGCC and supercritical PC plants for achieving approximately 90% CO_2 capture are reported In Table 5. The improved economic performance results largely from the lower energy penalty incurred by IGCC than for PC when CO_2 removal is required.

Chen and others (2006) reported that there are no generally available process models that can be easily used or modified to study the performance and cost of CO_2 removal options from IGCC systems for different user-defined assumptions and technology selections. Reported cost data also are relatively limited and often incomplete, and uncertainties in performance and cost were seldom

Table 5 Performance and economic impacts of CO_2 capture on IGCC and PC plants (Nexant Inc, 2006)

	IGCC	Supercritical PC
Net plant output (pre-CO_2 capture), MW	425	462
Plant output derating, %	14	29
Heat rate increase, %	17	40
Total capital cost increase, %	47	73
Cost of electricity increase, %	38	66
CO_2 capture cost, US$/t	24	35

considered. They used the Integrated Environmental Control Model (IECM) which combines plant-level mass and energy balances with empirical data and process economics (Rubin and others, 2005). The effect of different CO_2 capture efficiencies on auxiliary power requirements, thermal efficiency, capital cost, cost of electricity and CO_2 avoidance cost was studied. For a plant using Selexol™ based CO_2 capture, the avoidance cost was lowest when the total CO_2 removal efficiency was in the range of 85–90%, which indicates that the optimal CO_2 capture efficiency is also in this same range.

The integration of different CO_2 capture technologies in a coal gasification plant was assessed by van Aart and others (2007). They calculated that with CO_2 capture the net efficiency was reduced by 9.3% to 40.3% (LHV).

In early 2006, RWE Power announced a plan to build a commercial lignite fuelled IGCC plant with carbon capture (Wolf and others, 2007). Commissioning was planned for 2014. In the early concept development phase, the calculated net efficiency was far lower than had been expected for IGCC technology, ranging from 39% to 45% (LHV), just about equal to modern conventional steam plants. This was mainly due to optimising the plant for carbon capture and storage. In the CCS mode, the efficiencies were calculated to range from 35–38.5% with specific CO_2 emissions of 90–280 g/kWh and capture rates of 91% and 75% respectively. The target efficiency had been 40%. Thus, the results of the concept development phase showed that an IGCC plant with CCS will be much more expensive than indicated by other studies.

A detailed techno-economic assessment of both the Shell and GE IGCC systems was carried out by Huang and others (2007, 2008). Their simulations revealed that all the CO_2 capture cases resulted in large decreases in thermal efficiency with significant cost penalties in terms of both specific investment and electricity production cost. Efficiency losses between 8.5% and 10.7% were registered for the corresponding CO_2 capture options studied. Even more significant was the impact of CO_2 capture on the economics, resulting in an electricity cost increase between 38% and 42%.

Higher efficiencies and lower electricity generation costs were associated with the sour shift systems in connection with both technologies. Based on a sour shift system, the CO_2 avoidance cost of the Shell system, which ranged from 27 to 30 $/t, was around 10–11% lower than the GE system.

These figures are fairly close to those reported by Ciferno (2007) for plants capturing the CO_2 using the Selexol™ process. The increased cost of electricity for the Shell plant was 37% and 32% for the GE plant. The CO_2 capture energy penalty was 9.1 percentage points for Shell and 5.7 for GE.

Shell's own studies indicated that, adding conventional technologies to IGCC for pre-combustion carbon capture reduces the efficiency by approximately 11%. It was noted that this number is higher than other studies (Prins and others, 2009). Their medium- to long-term aspiration is to design an IGCC power plant with >90% carbon capture, and a coal-to-power efficiency of 45%. The relative capital expenditure increase due to carbon capture was estimated to be ~29%. This number excluded investment in logistics and storage of carbon dioxide, wellheads, and any related infrastructure.

Within IGCC technologies there are different methods of capturing the CO_2. Six physical and chemical process were modelled using Aspen Plus™ software by Kanniche and Bouallou (2007). After a selection based on energy performance, three processes were selected and studied in detail: two physical processes based on methanol and Selexol™ solvents and a chemical process using activated methyldiethanolamine (MDEA). For an 'advanced' IGCC operating at high pressure (6.4 MPa) they assessed only methanol solvent capture. The higher pressure favours physical absorption. The results showed that the basic generating cost from 'classical' IGCC with capture would increase by 39% relatively to 'classical' IGCC without capture. The incremental production cost induced by CO_2 capture for 'advanced' IGCC was only 28% which leads to a relatively lower cost per tonne of CO_2 avoided which was 82% lower in the case of 'advanced' IGCC than in 'classical' IGCC. Absolute values of cost estimates were not provided and it was suggested that those given elsewhere should be viewed with caution. Kanniche and others (2009, 2010) pointed out that the technical and economic estimates presented in their work were not sufficient alone to determine the choice of a system for the capture of CO_2. Constraints related to resources such as fuel and water may also influence this choice. Therefore, it appears difficult to make a once-and-for-all decision about the 'best CO_2 capture process'. However, the results of their studies suggested that pre-combustion capture by physical absorption (methanol) should be used for IGCC.

Descamps and others (2008) evaluated the efficiency of an IGCC plant using methanol for CO_2 capture. One attraction of the methanol process is that the required energy consumption is moderate for this operation compared with chemical absorption. They found that an important aspect of CO_2 capture is the energy amount required by auxiliary systems. This energy consumption reduces the overall efficiency of power generation, typically, by 8–12% (difference between the efficiencies without and with CO_2 capture).

Several cases of technical design, the performance and an economic evaluation for IGCC power plant concepts with and without CO_2 capture operated on world market hard coal and German lignite were evaluated by Gräbner and others (2009, 2010) as part of the German COORIVA project. It was calculated that the IGCC power plants without CO_2 capture would have net efficiencies (LHV) of 45.9% (hard coal) and 51.5% (lignite). The loss in efficiency due to CO_2 capture constituted 11.0 percentage points for hard coal and 10.2 in the case of lignite. The capital costs of the IGCC power plants were assessed within a ±30% accuracy frame. In cases without CO_2 capture the capital cost comprised €2.01 billion (hard coal) or €1.95 billion (lignite) and increased by the addition of CO_2 capture to €2.15 billion (hard coal) or €2.22 billion (lignite). For hard coal the cost of electricity increased by 13.4% with the addition of carbon capture and for lignite by 11.8%.

As part of the German HotVeGas project a thermodynamic IGCC model was developed and verified by Kunze and Spliethoff (2009a,b; 2010) using Aspen Plus™ and Ebsilon Professional. The model incorporated improved technology and achieved an efficiency of 38.5% and 41.9% for hard coal and lignite, respectively. While the results were consistent with then current studies, it was suggested that major studies were too optimistic. Compared with the corresponding non-capture plant the efficiency drop was estimated to be approximately 10 to 12 percentage points.

A study analysing post-combustion and pre-combustion carbon dioxide capture options using gas-liquid absorption processes in physical and chemical solvents was carried out by Cormos and others (2009). Three plant configurations were analysed in detail by modelling and simulation:

- conventional IGCC technology, no carbon capture;
- IGCC technology, carbon dioxide pre-combustion capture using physical absorption (Selexol™), 90% carbon capture rate;
- IGCC technology, carbon dioxide post-combustion capture using chemical absorption (MDEA), 90% carbon capture rate.

Comparing IGCC scheme without carbon capture (Case 1) with the same technology but with a carbon capture step (case 2 – pre-combustion capture and case 3 – post-combustion capture), the penalty in overall plant energy efficiency of the carbon capture process is about 6.33% for the case of pre-combustion capture (case 2 versus case 1) and 7.52% for the case of post-combustion capture (Case 3 versus Case 1). For gasification technologies, the pre-combustion capture technology has a lower energy penalty compared with post-combustion capture (about 1.2% in terms of net energy efficiency). This is explained by the fact that carbon dioxide concentration in the syngas (about 40 vol%) and syngas pressure (about 3 MPa) is much higher compared with the post-combustion case when carbon dioxide concentration in the flue gas is about 8–10 vol% and the pressure is close to the atmospheric pressure. The main conclusion of the study was that pre-combustion carbon dioxide capture method is more suitable for gasification processes than post-combustion capture (lower energy penalty, possibility of cogenerating power and hydrogen, higher degree of plant flexibility, etc). Later studies also compared the use of MDEA as a pre-combustion solvent; it was reported that post-combustion capture using MDEA is slightly less efficient in terms of net electrical efficiency compared with pre-combustion capture using the same solvent (Cormos and others, 2011a,b; Cormos, 2011).

An economic evaluation of an IGCC power plant with CCS in China has been reported by Zhaofeng and others (2011). A new virtual IGCC-CCS power cycle was defined and compared with a reference plant based on the GreenGen project (*see* Section 7.1). In contrast to the reference case using a gas turbine fuelled with syngas and without CO_2 capture, the virtual power cycle was made up using a generic hydrogen-burning gas turbine subsequent to an integrated gas separation unit in which CO_2 is removed (jointly with H_2S). Cost analyses suggested that pre-combustion carbon capture is not justifiable from mere commercial reasoning, as the inclusion of CCS cannot provide profit under the current energy regime in China. Net COE for the IGCC-CCS was calculated to be more than 60% greater than for the reference plant. It was emphasised, however, that the analyses were based on a first-of-a-kind plant, which is far more expensive than conventional power generation, and also because the size of plants are smaller than the economically optimal size.

An analysis of coal-fired gas turbine plants with carbon capture has been carried out by Birley and others (2011). Seven plant configurations were analysed for different energy market scenarios with regard to:
- plant integration (water and steam interfaces between gas island and power island),
- syngas cooling;
- carbon capture rate;
- synthetic natural gas (SNG) synthesis.

Some of the results from the study included the findings that:
- the availability is 89–90% for all concepts which is acceptable for power plants;
- net efficiencies of 35–37% are expected values for CCS plants.

Most importantly however, none of concepts were found to be economically feasible in all considered scenarios. SNG production was found to be not feasible, as SNG export is cost prohibitive in all the scenarios studied. It was concluded that he key to economic plant operation is to lower specific investments rather than to raise efficiency.

6.1 Sorbents

A preliminary study was carried out by Kakaras and others (2005, 2006) in which they compared IGCC systems using Selexol™ based CO_2 capture and a regenerated CaO based capture in the gasifier. They concluded that the integration of the coal gasification, CO shift reaction, and CO_2 capture in one single reactor results in an optimised low carbon fuel gas production with decreased energy and efficiency penalties. The net efficiency of a lignite based IGCC plant with CaO based CO_2 capture was estimated to be 36.2% compared with 34% for an IGCC with Selexol™ based absorption. It was noted that the make-up $CaCO_3$ that is required due to the decay of the sorbent should also be added to the electricity costs. However, taking into account the significantly higher efficiency, the electricity cost of the IGCC with lime CO_2 capture was expected to be lower than that of the IGCC with Selexol™ CO_2 removal. Based on simulations using Aspen Plus™, Klimantos and others (2006) found that net plant efficiencies between 36% and 38% (LHV) were possible for both technologies. They pointed out that the main advantage of the physical absorption process is that is based on almost commercially available technology. From a thermodynamic point of view the process based on in situ capture exhibits promising performance and probably higher plant efficiencies could be achieved. It was noted however, that there are many technical barriers that should be overcome such as the cyclic stability of CaO based sorbents which constitute a crucial factor for the thermodynamic performance of this concept.

An environmental assessment and extended exergy analysis (EEA) of a hydrogen-fed steam power plant in which the H_2 is produced by a zero CO_2 emission coal gasification process (the ZECOTECH© cycle) was carried out by Corrado and others (2006). The CO_2 capture is based on a regenerated CaO process producing CO_2 for a downstream mineral sequestration process. EEA differs from life cycle assessment (LCA) in that it includes all externalities – labour, capital and environmental costs. The mechanical section of the plant has a fuel-to-electricity efficiency of 50.7%. Here, the input is the syngas (composed of H_2 and steam), and the output is the electricity. The power plant as a whole (chemical+mechanical sections) has an overall exergy efficiency of 41.8%. The accounting of external costs using EEA showed that the real exergy efficiency of the system (in terms of primary resource exploitation) decreases from 41.8% to about 17% if CO_2 capture and sequestration is included. The exergy efficiency decrease is due to the assumption that 30% of the energy output of ZECOTECH© is used by the mineral sequestration process. EEA, in addition, includes the exergy equivalent of the additional installation costs, quantified as 10 €/t of sequestrated CO_2.

Possible optimal configurations of the ZECOMIX plant (*see* Section 7.1) were reported by Calabrò and others (2008). In this coal hydrogasification plant the CO_2 capture by a CaO based sorbent is integrated into the methane reformer. They considered two possible plant flowsheets: ‘plant 1’, which is the base case, and ‘plant 2’ which differed from each other with regard to the calciner island for the regeneration of the sorbent. In ‘plant 1’ configuration the calciner is fuelled by coal and the calcination process is performed at atmospheric pressure by means of flue gas produced by the oxycombustion of coal. Hence, the sorbent regeneration is conducted at a different pressure with respect to the CO_2 separation process (3 MPa) and there is a need for solid circulation between the carbon capture unit (CCU) and the calciner. In ‘plant 2’, a part of the raw syngas leaving the gasifier is fed through the calciner. The heat needed to regenerate solid sorbent is obtained from the flue gases released from burning the raw syngas in an oxygen stream. As a result, the regeneration process is conducted at a pressure equal to the pressure of the CCU and no pump for solid circulation is needed. It was recognised that a major drawback of the ‘plant 2’ option is the higher steam demand of calciner. In fact, due to the higher operating pressure, steam is injected into the calciner to reduce partial pressure of CO_2. As a result, ‘plant 1’ with an atmospheric calciner was found to be the more promising technology option achieving a higher overall efficiency in the vicinity of 50%.

A detailed analysis of the thermodynamic aspects of the process was carried out by Romano and Lozza (2010). They found that, depending on sorbent utilisation, a net plant efficiency of 44–47% (LHV) with a virtually complete carbon capture could be obtained. Unless CaO exiting the plant could be used as by-product, low CaO utilisation is consequently highly detrimental to plant performance. They conceded that the high complexity of the chemical island and the importance of a good sorbent performance should however be taken into account for a fair comparison with other plant concepts.

The techno-economic evaluation of four novel IGCC power plants fuelled with low rank lignite coal with a CO_2 capture facility has been investigated using the ECLIPSE process simulator by Mondol and others (2009). The performance of the proposed plants was compared with two conventional IGCC plants with and without CO_2 capture. The proposed process was based on the Absorption Enhanced Reforming (AER) reaction that combines steam gasification of lignite, with the high temperature removal of CO_2 by using high temperature efficient sorbent materials, namely CaO. The results show that the proposed CO_2 capture plants efficiencies were 18.5–21% higher than the conventional IGCC CO_2 capture plant. For the proposed plants, the CO_2 capture efficiencies were found to be within 95.8–97%. The CO_2 capture efficiency for the conventional IGCC plant was 87.7%. The specific investment costs for the proposed plants were between 1207 and 1479 €/kWe and 1620 €/kWe and 1134 €/kWe for the conventional plants with and without CO_2 capture respectively. It was admitted however, that the advanced technologies are not currently available in the market leading to difficulties in accurately estimating their capital costs.

Sorbent flow ratios have important effects on the system net efficiency for the IGCC power plant using the calcium looping cycle (Y Li and others, 2011). In order to capture CO_2 efficiently, there is a need for a fresh feed of sorbent to compensate for the decay in CO_2 capture activity during long-term cycles. The system power generation net efficiency increases with CO_2 capture capacity of the calcium-based sorbent. Conversely, the system power generation net efficiency will decrease due to more energy and sorbent consumption in the calciner. Thermodynamic simulation of an IGCC system using a limestone modified with acetic acid solution to help it retain high reactivity showed much higher CO_2 capture efficiency and system net efficiency than those using the natural limestone sorbent at the same flow ratio. The system net efficiency using the natural and modified limestones was 41.7% and 43.1%, respectively, at a CO_2 capture efficiency of 90% without the effect of sulphation. Sulphur in the char has adverse effects on CO_2 capture efficiency and system net efficiency.

6.2 Membranes

Chiesa and others (2006) compared the power balance and performance of three different power plants based on IGCC technology:

- a conventional IGCC plant where CO_2 is vented to the air;
- a low CO_2 emissions IGCC based on commercially available technologies (that is, acid WGS reactors convert CO to CO_2 that is removed by a Selexol™ physical absorption process);
- a plant based on the hydrogen separation membrane reactor (HSMR) technology.

The comparison showed that the HSMR configuration achieves a significantly higher efficiency than the Selexol™ process, in addition, can capture only 90.4% of the carbon contained in the input coal, against the complete removal allowed by the HSMR plant. Two main reasons explain the better performance of the HSMR plant:

- the lower power required by the CO_2 compressor (since the CO_2 stream is available at about the gasification pressure while in Selexol™ process CO_2 is released during the regeneration phase in the range 0.1–0.8 MPa);
- the lower steam flow rate extracted for promoting the WGS reaction.

The cost of CO_2 avoided in \$/tCO_2, was calculated to be 32.55 for the Selexol™ process as against 23.27 for the HSMR. However, a study by De Lorenzo and others (2008) concluded that plants employing HSMRs appear to have efficiencies and economics that are comparable with those of analogous plants that employ more conventional gas separation technologies (Selexol™ absorption of CO_2 and H_2 purification with pressure swing absorption). The expected gains due to a continuous removal of H_2 in a HSMR are present but do not significantly improve the economics of the plant. It was noted that this situation may tilt in favour of HSMR-based systems that are built around advanced membranes with H_2 permeances that are dramatically higher than that used in their calculations.

Amelio and others (2007) have suggested that the traditional shift reactors and the physical adsorption unit in an IGCC can be replaced by catalytic palladium membrane reactors (CMR). Using a computational model their analysis showed that the membrane plant was more economic than the WGS/adsorption plant. Their COE was calculated to be 61.20 \$/MWh compared with values reported in the literature for IGCC systems with 'traditional' CO_2 capture systems in the range of 54 to 79 \$/MWh. However, their calculations also revealed a 'rather moderate' performance penalty of a membrane plant with respect to the traditional IGCC . There was a 3.46% penalty in efficiency and a 3.48% penalty in net power, fundamentally due to the higher electrical power consumption for the CO_2 compression and for the production of the steam used as the sweep gas for the membrane reactor.

Published data for an operating power plant, the ELCOGAS 315 MWe Puertollano plant, was used as a basis for the simulation of an IGCC process with CO_2 capture by Grainger and Hägg (2008). This incorporated a fixed site carrier polyvinylamine membrane to separate the CO_2 from a CO shifted syngas stream. It appears that the modified process, using a sour shift catalyst prior to sulphur removal, could achieve greater than 85% CO_2 recovery at 95 vol% purity. The efficiency penalty for such a process would be approximately 10 percentage points, including CO_2 compression. A modified plant with CO_2 capture and compression was calculated to cost 2320 €/kW, producing electricity at a cost of 7.6 c/kWh and a CO_2 avoidance cost of about 40 €/tCO_2. The lifetime of the evaluated membrane is unknown. A continuous run lasting four weeks indicated that the membrane was stable, but long-term testing with real gas feeds would be required to establish the operating lifetime. It was assumed for the economic evaluation that the membrane modules must be replaced every five years.

Process simulation using Aspen Plus™ under several scenarios including IGCC with no CO_2 capture, IGCC with Selexol™, and IGCC with a polybenzimidazole (PBI) membrane separator were carried out by Krishnan and others (2009; *see also* O'Brien and others, 2009). In the three scenarios, the simultaneous CO_2 and H_2S capture using the high temperature membrane appeared to have the lowest COE. However, this mode of capture will require the development of membranes that are not permeable to H_2S. If H_2S permeates through the membrane and it needs to be captured using a solvent such as Selexol™, then the estimated costs of electricity between the membrane- and Selexol™ based systems are very similar. However, it was pointed out that this result is based on preliminary membrane data while the operation of Selexol™ has been optimised over many years. Additionally, no steps were taken to optimise the membrane separation parameters.

A cost comparison carried out by Plunkett and others (2009a,b) compared hydrogen membranes with conventional physical solvents. NETL target costs were used for the membranes due to the their early stages of development. It was concluded that hydrogen membranes have the potential to significantly improve overall IGCC plant efficiency and cost compared with conventional physical absorbent systems. Hydrogen membranes can produce CO_2 at high pressure, significantly reducing CO_2 compressor power needs. From an IGCC cost perspective, the analysis found that hydrogen membranes, in combination with warm gas clean-up, have the potential to reduce COE by 10–15% compared with conventional physical absorption. These costs rely on attaining NETL target costs for the hydrogen membrane system. If these target costs cannot be attained when commercialised, the resulting COE will be correspondingly higher. Gray and others (2010; *see also* Ciferno and others, 2011) calculated that the combined benefits of warm gas clean-up and the hydrogen membrane contribute 40% of the efficiency benefit and 30% of the COE reduction. The plant efficiency increases by 2.9 percentage points from 33.3% for a plant with warm gas clean-up and capture by Selexol™ to 36.2% for the hydrogen membrane plant. The increase in process efficiency in the carbon capture scenario was attributed to eliminating the Selexol™ reboiler and auxiliary power, and also producing CO_2 at elevated pressure thus reducing CO_2 compressor load. Compared with the Selexol™ process, CO_2 separation via the hydrogen membrane was projected to reduce the levelised cost of electricity (LCOE) from 0.1000 $/kWh to 0.0880 $/kWh – a decrease of 12%.

The techno-economic characteristics of physical absorption and water gas shift reactor membranes, were studied using the chemical process simulation package 'ECLIPSE' by Rezvani and others (2009) and compared with a conventional reference case. The power plant characteristics of the IGCC with CO_2 capture using physical absorption were nearer to the reference case. This was shown in a multivariate analysis using the principal components. However, the membrane-based option also performed well in the assessment.

Novel CO_2 and H_2 selective membrane-enhanced WGS processes were compared with a baseline gasification process for coal based hydrogen and power cogeneration by Li and Fan (2010). Again, NETL target costs were used for the membrane systems. It was found that the CO_2 selective membrane system, although better performing than the baseline gasification system using Selexol™ or MDEA, still had drawbacks. There is a need for an additional step to purify H_2 and high steam consumption in the purging step. In addition, the study had assumed a perfect membrane with 100% selectivity. Because the actual selectivity of a CO_2 selective membrane is often much lower, the performance of the CO_2 selective membrane system can he further penalised by the potential requirement for additional CO_2 purification steps. The H_2 selective membrane system was judged to be the better choice, although it was admitted that the cost and performance uncertainty of this novel process could he high.

A structured exergy analysis of an IGCC plant with carbon capture has been carried out by Kunze and others (2011). The investigated base case IGCC showed an exergy efficiency of 40%. It was found that 80% of the corresponding losses are related to just four devices: gas turbine, gasifier, acid gas removal (AGR), and CO shift. An advanced IGCC plant based on a new hot gas clean-up concept was introduced. The new concept showed a significant loss reduction potential of 5.2 percentage points compared with the base case using methanol to capture the CO_2. Due to the membrane enhanced shift conversion at a substantially higher temperature level the hot gas clean-up concept is closer to the ideal conditions and consequently exergetically favourable. It was assumed that due to the continuous separation of the produced hydrogen, the water to CO ratio can be reduced significantly and that the required CO conversion rate can be maintained even at increased temperatures. In addition, the membrane was assumed to be resistant to sulphur components in the syngas.

Aspen Plus™ modelling carried out by Ku and others (2011) indicated that the energy efficiency penalty associated with CO_2 capture using conventional liquid solvents is 6.7 points. The use of a membrane can reduce this penalty to 5.0 points, provided the membrane can recover 90% of the H_2 in the shifted syngas feed. The net benefits accrue from the avoided need for reheating of the fuel after the H_2/CO_2 separation, and the reduced CO_2 compression loads, due to the higher recovery pressure of the CO_2. However, reducing the H_2 recovery by the membrane erodes these benefits. This is because the power produced by the catalytic oxidiser does not quite offset the reduced gas turbine output. At 70% H_2 recovery by the membrane, the net thermal efficiency penalty is 7.0%, making the membrane-based solution unfavourable compared with the conventional liquid solvent system. This trend suggests that the highest possible H_2 recoveries are desirable, to maximise the power generation by the gas turbine. However, it was pointed out that the catalytic oxidiser cannot be completely eliminated. This is because one inherent limitation of the membrane approach is its inability to recover the non-H_2 fuel components from the feed stream. Since no known membrane materials exhibit significantly higher transport rates for CO and CH_4 over CO_2, downstream operations on the retentate stream are needed to recover the energy from CO, CH_4 and unrecovered H_2.

The capital costs of a conceptual full-scale membrane module were calculated by Dolan and others (2010). The module was a two-sided planar (2000 × 100 mm) mounted in a cylindrical containment vessel with 80% packing density. The cost of a 50 µm Pd membrane was $2090 per module and for a 40 µm Pd-Ag membrane this fell to $1672 per module. It was suggested that membrane costs appear prohibitive.

An evaluation of CO_2 and H_2 selective polymeric membranes for CO_2 separation in IGCC processes was carried out by Franz and Scherer (2010) using Aspen Plus™ modelling. The results for H_2 and CO_2 selective membranes showed that with state-of-the-art membranes (CO_2/H_2 selectivity 15.5, H_2/CO_2 selectivity 5.91) the current requirements concerning CO_2 purity and CO_2 separation degree cannot be fulfilled. A CO_2/H_2 selectivity of 150 for a single CO_2 selective membrane would be needed to obtain power plant efficiency losses below 10 percentage points with separation degrees above 85%. For H_2 selective membranes with a H_2/CO_2 selectivity of 50, separation degrees of 85% at efficiency losses below 10 percentage points can be reached. A later study by Franz and Scherer (2011) based on H_2 selective ceramic membranes indicated that selectivities above 440 are required for purities of the CO_2 stream of 95%. They showed that, for ceramic membranes with a selectivity of H_2 versus N_2 and CO_2 of 500, sour CO shift and sweet CO shift efficiency losses of 9.07 and 9.43 percentage points are feasible, respectively, while separating about 97% of the CO_2 with a purity of 95%. The difference between the sour and sweet CO shift cases was relatively small, so that the sweet concept may be preferable with respect to membrane operation safety (soot formation). A ceramic membrane reactor concept with simultaneous CO_2 separation and CO shift was the third carbon capture concept investigated. This concept achieves separation degrees of 96.6% and purities above 95% with an efficiency loss of 6.7 percentage points.

H_2/CO_2 selectivity estimated by Ku and others (2011) for IGCC ranged from about 20 to 60, considerably lower than for industrial H_2 production. At a 90% overall CO_2 capture rate, the required

H_2/CO_2 selectivity drops from about 60 to about 20 as the H_2 recovery is reduced from 90% to 70%. H_2/CO_2 selectivities of order 10–100 in the 250–400°C range are well within the capabilities of a wide range of materials, including ceramics, composites, and some polymers.

The Electric Power Research Institute (EPRI) has been working with the Canadian Clean Power Coalition (CCPC) on a roadmap for technological improvements to IGCC plants based on Canadian subbituminous coal as a feedstock (Schoff and Butler, 2011). The value of technology development was evaluated by discussing plant performance estimates developed by EPRI and the supporting technology suppliers. The most significant improvements in plant performance came from larger, more efficient gas turbines. These showed a net plant efficiency improvement ranging from 2 to 5 percentage points (HHV). The next most significant benefit came from the hydrogen membrane technology, which showed approximately 2 percentage points improvement compared with capture using Selexol™ when excluding the effect of the high temperature/pressure sulphur recovery system installed upstream.

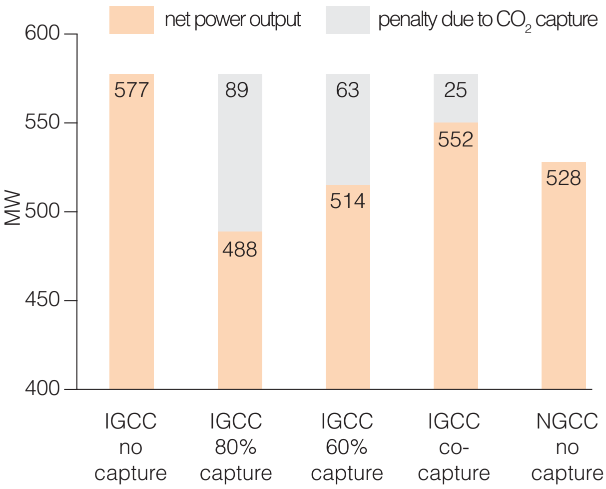
6.3 Co-capture of H_2S

A technical and economic comparison of the performance of five plant designs in the 500 MW output range was carried out by Ordorica-Garcia and others (2006): IGCC without CO_2 capture, IGCC with 80% capture using glycol, IGCC with CO_2 emissions equal to those of a natural gas combined cycle (NGCC), IGCC with CO_2 and H_2S co-capture, and NGCC without capture. Aspen Plus™ models were developed to simulate the plant performance. The IGCC plant models were based on the use of Canadian subbituminous coal. The simulation results showed that the economics favour higher capture levels in new IGCC plants. The CO_2 mitigation costs corresponding to IGCC plants with 80% capture were slightly lower than those corresponding to IGCC plants with equal emissions to those of NGCC plants (28 versus 30 US$/t$CO_2$ avoided). The capital cost difference (per kW of net installed capacity) between those plants was 7%, while the CO_2 emissions of the former were almost half those of the latter. IGCC plants with CO_2 and H_2S co-capture were found to have substantial techno-economic advantages over IGCC plants that capture CO_2 and H_2S separately. Based on a 577 MW IGCC, the power output decreases only to 552 MW for the co-capture case, whereas it drops to 488 MW when CO_2 and H_2S are captured separately. The incremental capital cost of co-capture plants is 6%, and their electricity production cost increase is less than half a cent, with respect to an IGCC without capture. The CO_2 mitigation cost of co-capture plants is at least four times lower than their separate CO_2 and H_2S capture counterparts. Figure 8 shows comparisons of power output and thermal efficiency (HHV).

Similarly, a detailed techno-economic analysis of both the Shell and GE IGCC systems found that both systems with CO_2 capture are able to benefit from the use of the sour shift option in which the CO_2 and the H_2S are captured together in a single stage. The sour shift option avoids cooling and reheating the fuel gas before shift conversion, which results in a better process performance and lower specific investment than for the sweet shift option. Sour shift gives better process efficiency than sweet shift (Huang and others, 2007).

The performance of SEWGS applied to IGCC was investigated by Gazzani and others (2011). First, two IGCC reference cases based on dry feed slagging Shell gasifier, with and without CO_2 capture, were defined. Then, two different integrations of SEWGS were investigated. The first assumes a conventional low temperature acid gas removal process upstream of the SEWGS; this solution shows slight thermodynamic advantages towards the reference case with CO_2 capture (higher efficiency of 1 percentage point), but not from layout simplification and equipment savings. The second solution assumed a simultaneous CO_2 and sulphur separation from the syngas; this resulted in a net electric efficiency gain over the reference case of about 2 percentage points. The lower efficiency of the sweet shift case of about 1 percentage point was because the syngas has to be cooled down to ambient temperature.

a) Power output comparison



b) Efficiency comparison

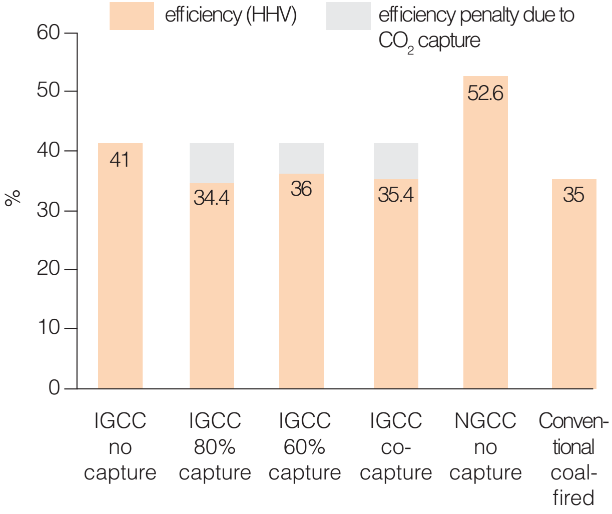


Figure 8 Power output and efficiency comparisons (Ordorica-Garcia and others, 2006)

Air Products have recognised that a H_2 pressure swing absorption (PSA) technology adapted to handle sour feedgas (sour PSA) would enable a new and enhanced improvement to a gasification system (Hufton and others, 2011). The complete Air Products CO_2 capture technology for sour syngas consists of a sour PSA unit followed by a low calorific value sour oxycombustion unit, and finally a CO_2 purification/compression system. The adsorbents used in the sour PSA were not identified but it was claimed that it can achieve a higher level of CO_2 capture than the conventional absorption technologies at significantly lower capital and operating costs. Overall, the system is expected to reduce the cost of CO_2 capture by over 25%.

6.4 Hydrogen or electricity?

The performance of plants producing hydrogen rather than electricity has been examined by Chiesa and others (2005) who concluded that state-of-the-art commercial technology allows transferring to decarbonised hydrogen 57–58% of the coal calorific value (LHV) while exporting to the grid decarbonised electricity amounting to 2–6% of coal LHV. In contrast to decarbonising coal IGCC electricity, which entails a loss of 6–8 percentage points of electricity conversion when capturing CO_2 as an alternative to venting it, CO_2 capture for H_2 production gives rise to a minor energy penalty (~2 percentage points of export electricity, associated mainly with compression of CO_2 to make it ready for storage). Estimated results from an associated economic analysis by Kreutz and others (2005) showed that the costs for ~91% decarbonised energy (via quench gasification at 7 MPa) were about 6.2 ¢/kWh for electricity and about 1.0 $/kg (8.5 $/GJ, LHV) for hydrogen; these were, respectively, 35% and 19% higher than the corresponding energy costs with CO_2 venting. Referenced to these analogous CO_2 venting plants, the costs of CO_2 emissions avoided were ~24 $/t for electricity and 11 $/t for H_2. The reason for these costs being much smaller for H_2 than for electricity is because much of the equipment needed for CO_2 capture is already required for H_2 production with CO_2 venting.

Damen and others (2006) have noted that no complete review of state-of-the-art and advanced technologies for both electricity and hydrogen production with CO_2 capture was available that allowed a comparison of these options on a common basis. They performed a consistent comparison of state-of-the-art and advanced electricity and hydrogen production technologies with CO_2 capture using coal and natural gas. After a literature review, a standardisation and selection exercise was performed for the Netherlands and the North Sea area to get figures on conversion efficiency, energy production costs and CO_2 avoidance costs of different technologies, the main parameters for comparison. In the short-term, electricity can be produced with 85–90% CO_2 capture by means of

NGCC and pulverised coal combustion with chemical absorption and IGCC with physical absorption at 4.7–6.9 c/kWh, assuming a coal and natural gas price of 1.7 and 4.7 €/GJ. CO_2 avoidance costs are between 15 and 50 €/t CO_2 for IGCC and NGCC, respectively. In the longer term, both improvements in existing conversion and capture technologies are foreseen as well as new power cycles integrating advanced turbines, fuel cells and novel (high temperature) separation technologies. Electricity production costs might be reduced to 4.5–5.3 c/kWh with advanced technologies. However, no clear ranking can be made due to large uncertainties pertaining to investment and O&M costs although for the coal-fired cases, pre-combustion strategies seemed to be more promising than post-combustion strategies and oxyfuel combustion with cryogenic air separation. Hydrogen production was also found to be more attractive for low cost CO_2 capture than electricity production since CO_2 capture at hydrogen plants causes a relatively small increase in production costs compared with electricity plants. Coal gasification enables CO_2 capture with marginal additional investment costs and efficiency losses. Costs of large-scale hydrogen production by means of steam methane reforming and coal gasification with CO_2 capture from the shifted syngas are estimated at 9.5 and 7 €/GJ, respectively. Advanced autothermal reforming and coal gasification deploying ion transport membranes might further reduce production costs to 8.1 and 6.4 €/GJ. Membrane reformers enable small-scale hydrogen production at nearly 17 €/GJ with relatively low cost CO_2 capture. A chain analysis was performed by Damen and others (2007) for promising CCS options, incorporating a wide variety of technologies, infrastructural settings, hydrogen end-use markets and reference systems to study various CCS configurations under specific conditions and assumptions (for the Netherlands). The results indicated that the overall impact of CCS on CO_2 emissions and electricity production costs is significant. The impact of CCS on costs of centralised hydrogen production and supply is not as substantial as for electricity production. However, it was concluded that, although the CO_2 price required to induce CCS in hydrogen production is low in compared with most electricity production options, electricity production with CCS generally deserves preference as a CO_2 mitigation option. Replacing natural gas or gasoline with hydrogen produced with CCS results in mitigation costs over 100 €/t CO_2, whereas CO_2 in the power sector could be reduced for costs below 60 €/t CO_2 avoided.

In 2006 the European Union funded a programme called ‘Dynamis’ which aimed to design plants that generated electricity together with a limited amount of hydrogen from fossil fuels (Røkke and others, 2006; Tzimas and others, 2009; García Cortés and others, 2009). These plants were called ‘Hypogen’ plants. It was also envisaged that, as the hydrogen market develops, IGCC-Hypogen plants would need to produce much greater amounts of hydrogen. Thus, the plants should be able to vary the proportion of hydrogen-to-electricity (Cormos and others, 2007; Starr and others, 2007). It was observed that, since the production of hydrogen is more efficient than that of electricity, a small reduction in the net amount of electricity results in a much larger amount of hydrogen becoming available. Figure 9 shows that when 430 MWe of electricity is being produced, the amount of hydrogen corresponds to 50 MW_H. Halving the amount of electricity to 215 MWe results in an increase in hydrogen to almost 500 MW_H. An advantage of a Hypogen plant is that it can improve the part load efficiency of an IGCC plant. Because hydrogen can be stored when there is no immediate demand, such a plant can continue to operate at full coal throughput at all times. When electricity is not needed, the plant would generate all its energy as hydrogen and the ancillary plant and CO_2 capture system would continue to operate.

A pre-feasibility study of a flexible hydrogen-electricity co-production IGCC coal-fed plant with CO_2 capture and storage was carried out by Fantini and others (2007) for a plant to be installed in Italy. The plant configuration would allow the flexible production of electricity and hydrogen following the fluctuations of the market demand and price on an hourly basis. Results of plant steady-state modelling in different operational configurations showed that economic performances of co-production configurations were better than those that had only electric energy production, and increased with the ratio of produced hydrogen/electric energy.

A study was carried out by Foster Wheeler Italiana for the IEA GHG (2007) and was summarised by Arienti and others (2007). The study considered the possible advantages of hydrogen and electricity

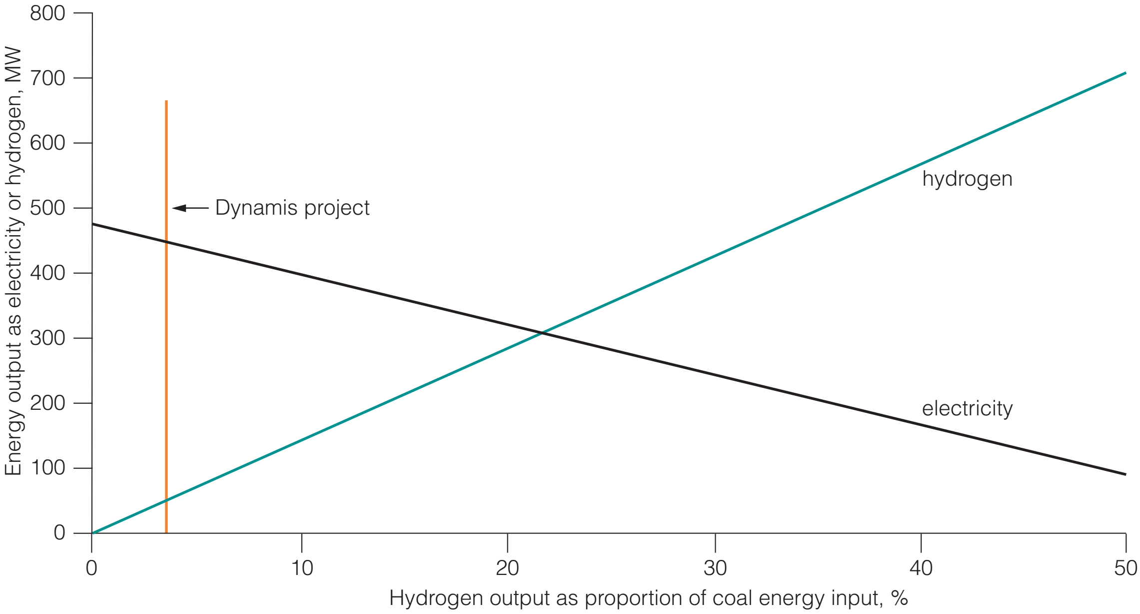


Figure 9 Hydrogen output as a proportion of coal energy input, % (Starr and others, 2007)

coproduction from coal with CO_2 capture. It was found that, assuming a constant hydrogen value, the COE in scenarios based on flexible coproduction plants and underground buffer storage of hydrogen was around 25% lower than in a scenario based on electricity-only and hydrogen-only plants without storage. However, differences emerged when the Netherlands were compared with the USA. Flexible plants without storage were advantageous in the USA because the peak demands for hydrogen and electricity are at different times of year. In the USA the differences in peak demand result in a higher plant load factor. This is not the case for the Netherlands where the peak demands for both are in winter. Updated cost figures were presented by Davison and others (2009, 2010) in which the original 25% value had reduced slightly to a 20% advantage for flexible coproduction plants.

The performances and costs of such plants in scenarios with various amounts of wind generation, based on data for power demand and wind energy variability in the UK were analysed by Davison (2009). He concluded that coal gasification, hydrogen production, pre-combustion capture of CO_2, underground buffer storage of hydrogen and combined cycle power generation has been shown to have substantial advantages over other CCS processes in future electricity systems which include large amounts of variable wind power generation. This process would avoid the need to vary the operating load of the gasification and CO_2 capture and storage equipment, resulting in significant operational and economic benefits. The percentage CO_2 capture in such hydrogen plants could be 98–99%.

The energy and exergy efficiencies of a conventional IGCC power generation system were compared with that of coal gasification-based hydrogen production system which uses WGS and membrane reactors by Gnanapragasam and others (2010). Their preliminary thermodynamic analysis suggested that the syngas-to-hydrogen system offers 35% higher energy and 17% higher exergy efficiencies than the syngas-to-electricity (IGCC) system. The specific CO_2 emission from the hydrogen system was 5% lower than IGCC system. The extra electrical power consumption for compressing the exhaust gases to store CO_2 is above 70% for the IGCC system but is only 4.5% for the H_2 system due to the larger volume of exhaust gases in the IGCC system. However, it is important to note that the comparisons were for *downstream* post-combustion capture of the CO_2 and not for an IGCC with pre-combustion capture.

Although there seems to be general agreement that flexible coproduction of hydrogen and power is an attractive option, it is not quite unanimous. For example, Ku and others (2011) point out that, if hydrogen is not produced, the H_2/CO_2 selectivity of H_2 selective membranes could be lower if the permeate is combusted in a gas turbine as opposed to purified for industrial use. An evaluation of the economic effects of introducing flexibility into state-of-the-art integrated gasification cogeneration (IG-CG) facilities was carried out by Meerman and others (2011). The IG-CG facilities used eucalyptus wood pellets, torrefied wood pellets, and Illinois No 6 coal as feedstock and produced electricity, Fischer-Tropsch liquids, methanol and urea. Hydrogen production was not included however. The results indicated that feedstock flexibility does not improve the economics of these facilities. The main reason is the current high feedstock price for biomass compared to coal. Without a substantial CO_2 credit price it is not attractive to use biomass, therefore there is no need for feedstock flexibility. Furthermore, under the current market conditions, production flexibility between chemical and electricity production reduces the economics of the IG-CG facility. Only for the coal to methanol case were the production costs lower than the market price of the products.

6.5 Capture ready plant

Higman (2007b) argues that one of the main reasons why power producers are looking at IGCC for at least part their next generation of plant is that the technology is perceived as being ‘carbon capture ready’. He concluded that any developer would certainly be wise to conduct a study at the time of the original plant design, so that there is a clear understanding of what might be involved in a capture retrofit and a clear strategy for its implementation. It is conceivable that the performance of such a study could become a requirement for permitting the original plant. But, in his opinion, any such retrofit is unlikely to be required in the next ten years or so. Therefore the results of such a study must not be allowed to lock the developer into today’s technology. Rather, it should be considered as a baseline against which potential improvements in the future can be measured, when the retrofit has become necessary.

Five different types of IGCC plant in various stages of capture capability were studied by Alderson and others (2007). They ranged from an IGCC built for performance with no capture capability to one built for >85% capture and also retrofitted IGCC plants. It was found that a capture ready IGCC facility, employing a shift conversion stage, could be constructed at essentially the same unit capital cost as a conventional non-capture IGCC without shift. However, the increased cost lay in the loss of two percentage points in efficiency, resulting in higher feedstock costs and CO_2 emissions while the plant operates in non-capture mode. Converting this capture ready IGCC plant to capture operation could be achieved at an overall capital cost only marginally higher than that of a purpose-built capture plant. As noted above, converting a non-capture plant to capture operation involves major plant modifications which lead to the overall capital cost being significantly greater than the cost for constructing a capture ready plant and later adding capture.

6.6 Comparisons with other capture technologies

Holt (2006) has pointed out that, in the power industry, IGCC is generally perceived as not yet fully commercially proven, whereas capture of CO_2 from coal gasification derived syngas, via the shift reaction and subsequent CO_2 removal is commercially mature. In contrast PC plants are fully commercially proven but post-combustion CO_2 capture from PC plants is not proven at the scale needed for deployment.

Four of the leading technologies under development for capturing CO_2 emissions from coal-fired plant were compared by Maunder and others (2006) who considered the equipment, performance and economics of each technology. The technologies were:
- amine scrubbing of the flue gas of an advanced supercritical pulverised coal plant (SCPC);
- oxyfuel combustion firing of an advanced supercritical pulverised coal plant;
- IGCC;

- retrofitting existing gas-fed gas turbine power stations carbon-reduced gas fuel from an external gasification module.

The investment costs and COE were found to be comparable for all technologies and would be expected to reduce as the number of plants built increases. The net efficiencies of each of the technologies were also found to be comparable and these are expected to increase with technology developments.

The results of IEA GHG studies on the performance and costs of power plants with capture and storage of CO_2 were summarised by Davison (2007) The net efficiencies of the post-combustion capture, Shell IGCC and oxy-combustion coal-fired plants with capture were similar, 34.5–35.4% LHV. The efficiency reductions for CO_2 capture compared with the same type of plant without capture are 8.6–9.2 percentage points. The GE gasifier IGCC plant with capture had a lower efficiency, 31.5% (although an alternative design of the gasifier improved the efficiency by 1.2 percentage points).

However, this type of finding was denounced as a 'myth' by Ditzel (2007). He contended that CO_2 can be captured more efficiently from a concentrated gasifier's synthesis gas stream compared to a PC's flue gas stream, which is 100–150 times larger in volume. As a result, carbon capture from an IGCC will have lower efficiency losses, operating costs, and capital costs relative to a PC unit. Further, he added that, if an advanced lower-cost alternative for carbon capture from SCPC facilities is developed commercially, it is likely that the same (or a similar) technology can be applied to IGCC facilities at a proportionately lower cost thus maintaining IGCC's inherent cost advantage for carbon capture.

An IEA GHG (2006) report considered the future trends in the cost of CO_2 capture technologies for four types of electric power plants equipped with CO_2 capture systems: pulverised coal (PC) and natural gas combined cycle (NGCC) plants with post-combustion CO_2 capture; coal-based IGCC plants with pre-combustion capture; and coal-fired oxyfuel combustion for new PC plants. It was estimated that IGCC with CO_2 capture could have a higher overall cost reduction from learning than other coal-based power technologies because of greater cost reductions in the core power generation sections of the plant. However, the reduction in the incremental cost of capture in IGCC is lower than for plants with post-combustion capture. This report was summarised by Rubin and others (2007a). The estimates were based on nominal ('best estimate') learning rates for plant COE which showed a 3–5% decrease for each doubling of CCS plant capacity. Based on the study assumptions, IGCC plants with capture were found to have the highest projected learning rates for COE (nominally about 5%, ranging from 3% to 8%), while combustion-based plants had lower rates of learning (nominally about 3%, ranging from 1% to 5%). Combustion-based plants showed generally lower learning rates because a larger portion of their cost is dominated by relatively mature components. Table 6 shows the overall changes in COE based on the estimated learning rates. The largest COE reduction (18%) is

Table 6 Overall change in cost of electricity after 100 GW of capture plant capacity (Rubin and others, 2007a)

Technology	COE (excluding transport & storage)				
	Nominal, $/MWh			Range, $/MWh	
	Initial	Final	% change	Range	% change
NGCC plant	59.1	49.9	15.5	46.1–57.2	3.2–22.0
PC plant	73.4	62.8	14.4	57.8–68.8	6.2–21.3
IGCC plant	62.6	51.5	17.6	46.4–57.8	7.7–25.8
Oxyfuel plant	78.8	71.2	9.7	66.7–75.8	3.9–15.4

All costs in constant US$ 2002

seen for the IGCC system and the smallest (10%) for the oxyfuel system. In a study performed by van den Broek and others (2009), it was reported that, for IGCCs, the current installed capacity (~1.5 GW) was not sufficient to identify specific learning trends. With respect to the variables of energy use for CO_2 capture, it was not feasible to create learning curves due to lack of data. However, they confirmed the earlier finding that IGCC with carbon capture has the largest learning potential of the power plants with CO_2 capture. Under the condition that around 3100 GW of combined cycle capacity is installed worldwide, its efficiency improves from 33% in 2001 to 46% in 2050 while the efficiency of PC plants with carbon capture increases from 35% to ~42% over the same period.

Gerdes (2009; *also* Klara and Plunkett, 2010) has pointed out that adding CCS to an IGCC plant will add at least 30% to the COE according to NETL (2007). However, it is believed that, in the IGCC-CCS process alone, there is the potential to improve efficiency by 8 percentage points over conventional gasification and carbon capture technology, resulting in an efficiency of 39.8% (HHV). Capital cost reductions of more than 800 $/kW arising from less expensive technology alternatives were identified. It was suggested that advanced gasification based configurations are capable of generating electricity that is on par with current IGCC technology that does not capture carbon.

The types of coal used in PC and IGCC plants has been found to have a significant effect on both the absolute and relative costs of both systems (Rubin and others, 2007b). Their study showed that IGCC plants with CCS generally have a lower total COE than a similarly sized PC plant with CCS for bituminous coals, but for lower rank coals IGCC was either comparable in cost (for subbituminous coal) or higher in cost (for lignite). With low rank coals, the total water input for a slurry fed gasifier substantially lowers the gasification efficiency and increases the total system cost (Chen and Rubin, 2009). A probabilistic uncertainty analysis showed that most of the uncertainty in the total capital cost of an IGCC plant with CCS arose from uncertainty or variability in parameters for the basic IGCC system rather than the CO_2 capture system.

The US DoE National Energy Technology Laboratory used Aspen Plus™ simulation to compare cost and performance baselines for bituminous coal plants in a major study (NETL, 2010 – an update of the 2007 document). Their net thermal efficiencies (expressed on an HHV basis) were higher for the IGCC plants with capture (31.0–32.6%) than for a USC PC plant with post-combustion capture at 28.4%. The explanation was that the addition of CO_2 capture to the PC cases (Fluor's Econamine FG Plus process) has a much greater impact on efficiency than CO_2 capture in the IGCC cases. This is primarily because the low partial pressure of CO_2 in the flue gas from a PC plant requires a chemical absorption process rather than physical absorption. For chemical absorption processes, the regeneration requirements are much more energy intensive. Similarly, for capital cost, the average capital cost for IGCC CO_2 capture cases was 3568 $/kW, but for USC PC with post-combustion capture, it was $4070. The LCOE was calculated to be in the range 105.66–119.46 mills/kWh for the IGCC cases compared with 106.63 for the USC PC plant with capture (this was relatively lower than the figure used in the 2007 report). The total first year cost of CO_2 avoided was 52.9 $/t (average IGCC) and 69 $/t for USC PC, using analogous non-capture plants as the reference and 75 $/t (average IGCC), 69 $/t for USC PC using USC PC without capture as the reference. NETL (2011) has also studied the cost and performance of low rank coal IGCC cases.

As part of a feasibility study for IGCC technology to be located at a greenfield Texas Gulf Coast location, the cost and performance of IGCC was compared with a supercritical pulverised coal plant (SCPC) based on lower rank Powder River Basin (PRB) coal in a report issued by EPRI (2006). IGCC options included 100% PRB and 50/50 PRB/petcoke cases. The addition of CO_2 capture equipment also was evaluated as a retrofit for the 100% PRB IGCC and SCPC facilities. The Selexol™ system was used as the basis for the IGCC CO_2 capture technology, and the Econamine FG Plus K system was used for SCPC CO_2 capture technology. The findings were that installation of CO_2 capture equipment as a retrofit for both technologies results in a very significant decrease in plant output. IGCC net plant output decreases by approximately 25%, and the SCPC decrease in output is 29%. Likewise, the net plant heat rate of the facilities also increases by approximately 39% for the IGCC and 41% for the SCPC. Water consumption also is increased by approximately 23% for IGCC and 34% for SCPC. All these factors result in an increase of the levelised busbar cost by approximately 45% for the IGCC and 58% for the SCPC post-CO_2 capture. However, SCPC technology still provides the lowest busbar cost after CO_2 capture retrofit, although by less of a gap than pre-CO_2 capture. The avoided cost of CO_2 capture is less for an IGCC, implying that IGCC technology is the more economical choice for retrofit of CO_2 capture technology. It might be noted though, that there are very few coal fuelled IGCC plants that exist to be retrofitted. In addition, Alderson and others (2007) have pointed out that the insertion of a shift converter into an existing IGCC plant with no shift would mean a near total rebuild of the gasification waste heat recovery, gas treatment system, and the heat recovery steam generator, with only the gasifier and gas turbine retaining most of their original features. This raises the question of whether the conversion of an existing IGCC plant to capture CO_2 is really a retrofit operation.

Techno-economic comparisons of pre-combustion CO_2 capture and oxyfuel processes were carried out by Ekström and others (2009). Compared with the corresponding baseline power plants without CO_2 capture, net electric efficiencies were reduced with 6–9 percentage points for the IGCC pre-combustion capture technologies, oxyfuel PF and CFB technologies. Calculated electricity generation costs increase around 30–60% compared with the baseline power plants, with resulting CO_2 avoidance costs of around 10–40 €/t CO_2. The lignite-fired concepts all showed almost the same cost increases compared with their respective reference cases, For the bituminous coal cases, the calculated electricity generation costs and the CO_2 avoidance costs were lower for oxyfuel than for pre-combustion capture. It was suggested that the cost differences between pre-combustion IGCC and oxyfuel PF concepts for the same fuel are within the ranges of uncertainty that can be expected at the current level of development.

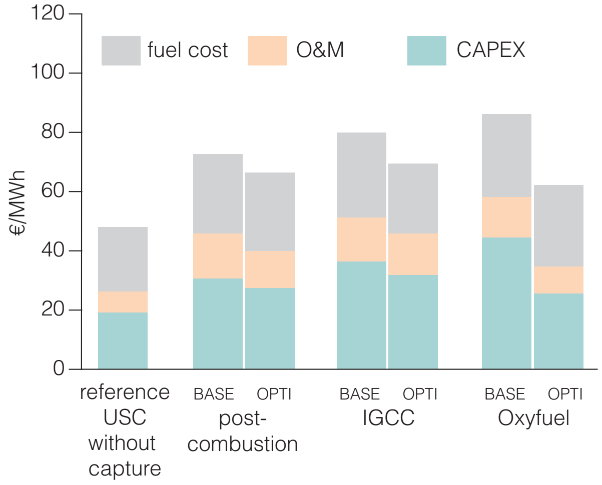
A report from EPRI (2011) presents essential cost and performance data on eight utility-scale power generation technologies drawn from ongoing research under the EPRI Technical Assessment Guide, Renewable Generation, and CoalFleet for Tomorrow Programs. Levelised costs of electricity were calculated based on methods generally consistent with those used in the EPRI Technical Assessment Guide. The latest LCOE estimates for IGCC and PC plants without capture show higher cost for IGCC at 68–73 and 54–60 \$/MWh respectively; however when capture is added, the COE estimates of IGCC and PC are very similar at 85–101 and 87–105 \$/MWh respectively.

In Australia, a pre-feasibility study which examined a 340 MW net IGCC power plant with carbon dioxide capture has been carried out (Wandoan Power Consortium, 2011; *see* Section 7.2). The study's financial modelling indicates that if the Wandoan project is developed with a grant funding contribution of AU\$ 1800 million applied to the construction phase then the project's LCOE is 192 AU\$/MWh in current dollars. This figure is much higher than the EPRI (2011) estimates but may reflect the local conditions in a fairly remote location in Australia since the study also indicated that a Wandoan sized 50 Hz IGCC plant with 90% CO_2 capture located in the US Gulf Coast region would cost 4798 US\$/kW. The incremental site specific cost of building the plant in Australia at Wandoan adds 4195 US\$/kW. The difference reflects a variety of factors including site ambient conditions (significantly warmer), local logistical requirements and local construction costs.

Best estimates of the costs for new power plants with CO_2 capture in Europe have been produced by the European Technology Platform for Zero Emission Fossil Fuel Power Plants (ZEP, 2011). The cost calculations made in the study utilised new, actualised data provided by the industrial and utility members of ZEP and reviewed by the working group, based on their own extensive knowledge and experience. This has enabled ZEP to estimate the LCOE and CO_2 avoidance costs for new-build commercial power plants with CO_2 capture that would enter into operation in the early 2020s, located at a generic greenfield site in Northern Europe. The cost estimates do not include any additional site-specific investments. Costs for CO_2 capture include the capture process, plus the conditioning and compression/liquefaction of the captured CO_2 required for transport. The technologies studied were first-generation capture technologies: post-combustion CO_2 capture; IGCC with pre-combustion capture; and oxyfuel for hard coal, lignite and natural gas, where applicable. The costs for the transport and storage of CO_2 were not included. For each technology, a range of costs was developed, with low-end costs based on more ambitious power plant designs that depend on a completely successful demonstration of the technology, the inclusion of technology improvements, refined solutions and improved integration. In the study, such plants were termed ‘OPTI’, which represents an optimised cost estimation. The more conservative, high cost plant designs were termed ‘BASE’ for a plant representing today’s technology choices, employing the most commercial designs while adopting a conservative approach to risk, component redundancy and design performance margins. All costs were referenced to second quarter 2009 investment costs. The results of the study were that, for a hard coal fired power plant (based on second quarter 2009, equipment cost levels and a fuel cost of 2.4 €/GJ), the addition of CO_2 capture and the processing of the CO_2 for transport will increase the LCOE from ~45 €/MWh to ~70 €/MWh, depending on the capture technology for a new-build OPTI power plant design. The CO_2 avoidance costs for capture were calculated to be in the range 30–40 €/t of CO_2 for an OPTI early commercial power plant design. The results are shown in Figure 10.

Although the results place the costs of IGCC with pre-combustion capture slightly higher than those of post-combustion capture, and oxyfuel appears to have a larger range of values with some studies indicating that this technology has the lowest cost, there is no clear difference between any of the capture technologies and all three could be competitive in the future, if successfully demonstrated. It was concluded that:

a) LCOE for hard coal-fired power plants with CO_2 capture



b) CO_2 avoidance costs for hard coal-fired power plants with CO_2 capture

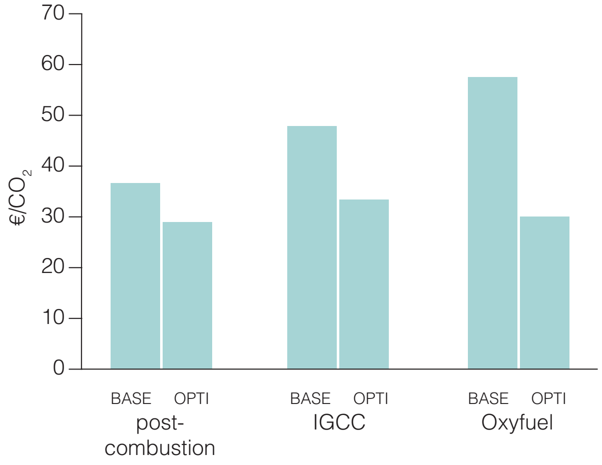


Figure 10 LCOE and CO_2 avoidance costs for hard coal fired power plants with CO_2 capture (ZEP, 2011)

> *In short, ZEP considers the costs determined in this study to represent the best current estimate for new-build commercial power plants with first-generation CO_2 capture technologies, entering into operation in Europe in the early 2020s.*

The IEA agrees that, for coal-fired power generation, no single CO_2 capture technology outperforms available alternative capture processes in terms of cost and performance (Finkenrath, 2011). An evaluation of techno-economic date for CO_2 capture from power generation revealed that average net efficiency penalties for post- and oxy-combustion capture are ten percentage points relative to a pulverised coal plant without capture, and eight percentage points for pre-combustion capture compared with an IGCC plant. In OECD regions LCOE increases for pre-combustion capture increases on average by 29 US$/MWh relative to an IGCC reference plant ranging from 19 to 39 US$/MWh. The relative increase of LCOE compared with the LCOE of the reference plant is on average 39%. Costs of CO_2 avoided are on average 43 US$/t$CO_2$ if an IGCC reference plant is used, ranging from 26 to 62 US$/t$CO_2$ for

OECD regions. However, if a pulverised coal plant reference case is used, average costs of CO_2 avoided rise to 55 US$/t$CO_2$. Estimated costs in China are lower at 32 US$/t$CO_2$, relative to a Chinese pulverised coal plant.

6.7 Comments

It is worth noting that, in the ZEP (2011) study, an IGCC plant without CO_2 capture was not selected as a reference power plant case because these types of plants have not been constructed in the last decade and the four existing IGCC power plants are best described as first-of-a-kind demonstration plants. No reliable cost data therefore exist.

As a consequence, the techno-economic studies considered in this chapter are mainly best guesses based on likely costs and also on the predicted performance of technologies that are yet to be fully developed such as hydrogen separation membrane reactors.

It is interesting to note that, near the beginning of the date range considered in this report, the investment costs, COE, and net efficiencies of the different CO_2 capture technologies were found to be comparable (Maunder and others, 2006; Davison, 2007). The most recent findings are remarkably similar (EPRI, 2011; ZEP, 2011). In economic terms no clear winner has yet emerged.

Even so, some remain to be convinced of the economics of IGCC with CCS. In an interview with PEi (2011b), Philippe Paelinck, Director of CO_2 Business Development at Alstom Power, expressed his opinion thus:

> *For producing power, integrated gasification combined-cycle (IGCC) is not the right answer. This technology has a very high capex, about twice that of a conventional coal plant, and that's without carbon dioxide capture. Moreover, it is not as flexible, available or efficient as a state-of-the-art pulverized coal (PC) plant. So IGCC is already a shaky and expensive proposal, and that's before any* CO_2 *capture consideration. We would therefore discard this option upfront. If the utility's plan is to go full capture from commissioning day, say in 2015, our recommendation today would be to go for an oxy-combustion plant. Our cost estimations show that this option is likely to be the most cost-competitive starting 2015.*

7 Pilot and demonstration plants

This chapter will look at pilot and demonstration plants that are operational or planned. It will also have a brief discussion of plans that have been abandoned. There are plans and proposals for other plants but there are also projects that have been abandoned.

7.1 Existing plants

There are some IGCC pilot and demonstration plants already in existence or under construction. A few of these are already in, or close to, operation of carbon capture units.

CO2CRC Mulgrave pilot plant

http://www.co2crc.com.au/research/demo_precombustion.html
An AU$5.5 million pre-combustion pilot plant has been sited at HRL's gasifier site at Mulgrave in Melbourne (Qader and others, 2009). The aim of the pilot plant was to map the operating windows of capture options (solvent, membrane, and adsorption) by investigating the separation performance of a solvent, a number of molecular sieving membranes at high temperatures, and identifying and testing suitable adsorbents over a range of temperature and pressure conditions. Results from the project have been reported by Anderson and others (2011). The gasifier is not fitted with a water gas shift reactor and hence the syngas produced from air-blown gasification of brown contains significant quantities of carbon monoxide (6.7 mol%) as well as 16.2 mol% CO_2 and 9.8 mol% H_2. Briefly, each technology was successful in demonstrating capture of CO_2 from syngas during three separate campaigns, which were completed from May 2009 until July 2010.

GreenGen 250 MW IGCC

www.greengen.com.cn/en
The GreenGen project is based in China – a 250 MW IGCC plant will be built in the initial stages, with capacity later expanding up to 650 MW (Cox, 2008; Shisen, 2008, 2009). The plant is sited at the LinGang Industrial Park in the Tianjin Binhai New Development Zone. Construction started in 2009. The third stage (2014-17) of the plans to build the GreenGen power plant include a 400 MW demonstration plant with large-scale hydrogen production from coal, hydrogen and gas combined-cycle power generation, and CO_2 capture and sequestration. The proposed 270 MW Good Spring IGCC project in New Jersey, USA, will use GreenGen technology and is intended to be carbon capture ready (http://www.emberclear.com/Good-Spring-IGCC.html).

Kemper County IGCC (Plant Ratcliffe)

http://www.southerncompany.com/smart_energy/smart_power_vogtle-kemper.html
Kemper County IGCC is currently under construction in Mississippi, USA, and is owned and operated by Mississippi Power. It is not a demonstration plant as such, rather it is 582 MW net coal-fired air-blown IGCC power plant at which 3.5 Mt/y of CO_2 is expected to be captured by Selexol™ in order to reduce carbon dioxide emissions by 65%, making it equivalent to a natural gas combined cycle plant. Construction commenced in June 2010 with operation expected in 2014. The plant will be fuelled with the local Mississippi lignite and has been allocated US$ 705 million from the US government. It is the first large-scale integrated project (LSIP) from the power sector to move into the Execute stage, representing a significant milestone for the large-scale demonstration of capture technology (GCCSI, 2011a,b).

Nakoso 250 MW IGCC demonstration plant

In Japan, construction of the 250 MW Nakoso IGCC plant began in August 2004 (Fujii, 2007). An IGCC design based on technology from Mitsubishi Heavy Industries Ltd (MHI) that uses a pressurised, air-blown, two-stage, entrained-bed coal gasifier and a dry coal feed system was selected.

Since the plant is air-blown, this results in a 50 mol% N_2 content in the syngas but this is considered advantageous as a good heat sink for the shift conversion. The CO_2 is to be captured using Selexol™ after a sour shift although it was noted that sweet shift appears more suitable for future CO_2 capture. This is because CO_2 removal after H_2S/COS removal can be performed using MDEA or Fluor solvent with flash regeneration. Selexol™ for sulphur only removal is less expensive than Selexol™ for H_2S and CO_2 removal. After completion of the design, construction and delivery of the plant, a series of demonstration tests were conducted at the Nakoso IGCC plant from September 2007 and proceeded on schedule successfully (Sakamoto and others, 2010). A feasibility study to execute a CCS demonstration project using the Nakoso IGCC plant has been in progress since April 2008. The Nakoso IGCC incurred severe damage mainly due to the tsunami after the earthquake off the coast of Japan in March 2011 (Watanabe, 2011).

Nuon Buggenum 253 MW IGCC plant

http://www.nuon.com/company/core-business/energy-generation/power-stations/buggenum/pilot-co2-capture.jsp

Nuon announced a pilot programme to install a pre-combustion pilot plant it its existing plant at Buggenum, the Netherlands, to be commissioned in August 2010. The pilot programme was to enable Nuon to acquire the knowledge and gain the experience necessary to apply carbon capture technology on a large scale at the planned Nuon Magnum plant (de Kler, 2008). The pilot plant was designed to treat 0.8% of the syngas produced by the main Buggenum plant and to capture approximately 10 kt of CO_2 per year (Gnutek, 2010). The pilot plant consists of five sections: syngas conditioning, water-gas shift condensate recovery, CO_2 absorption and solvent regeneration and CO_2 compression. The CO_2 absorption uses dimethyl ether polyethylene glycol (DEPEG) as a physical solvent. Recent developments have been reported by Damen and others (2011). The test and R&D programme has been divided into four work packages:

- plant operation and optimisation;
- water gas shift section;
- CO_2 absorption section;
- fouling and corrosion.

The modelling activities and catalyst experiments within the project have been initiated and the first results have been obtained. In January 2011, the pilot test programme, in which several test campaigns (with different catalysts, solvents and packing) are foreseen, was to start and will last for at least 1.5 years. Once the first data are gathered, model validation will start.

Puertollano

www.elcogas.es

One of the few IGCC demonstration plants currently in operation is the 335 MW plant at Puertollano in Spain operated by Elcogas S.A. (Casero and Garcia-Peña, 2006). Its design fuel is a mixture 50:50 poor quality coal (high ash content) and petcoke (high sulphur content). In 2005 the R&D department of Elcogas began a €19 million project on pre-combustion CO_2 separation technology. Brief details of the pilot plant implementation were provided by Casero (2007). A 14 MWth pilot plant for CO_2 capture and H_2 production, integrated in the 335 MW IGCC plant, operative by the beginning of 2009 was announced (Garcia Peña and Coca, 2009). The pilot plant consists of a WGS unit to convert CO into CO_2, a CO_2 separation unit based on absorption processes with amines (active methyldiethanolamine – aMDEA), and a H_2 purification unit (PSA) – all commercial processes. By March 2010 all the engineering work had been carried out, all the equipment had been supplied and the plant was 95% built (García Peña, 2010). It was proposed that the plant would be used to study WGS catalyst optimisation and test different catalysts, investigate new processes to separate CO_2-H_2, investigate different CO_2 treatment processes, and seek to improve the integration efficiency between the CO_2 separation processes and the IGCC plant. The plant was commissioned in June 2010 making it the first IGCC plant in the world to have a pilot plant at industrial scale to obtain H_2 and CO_2 ready for geological storage, integrated with electricity production. The cost of the pilot plant was €13 million, including design, construction, commissioning, and start-up suggesting capture costs in the range 18–22 €/t of CO_2 (Coca and García Peña, 2010). The first tonne of CO_2 captured was on 13 September 2010 and commissioning ended in October 2010. The plant treats 3600 m^3/h, 100 t/d, 2% of the total syngas generated in the power plant and can produce 2 t/d of 99.99% pure hydrogen with a CO_2 capture of >90% (García Peña and Coca, 2011a,b).

The main achievements and lessons learned from the pilot plant have been:
- Investment costs were lower than €13 million.
- Unexpected reactivity in first step of shifting unit since in design CO conversion into CO_2 was estimated to be of 85%, and 15% in the second step. However, in operation with a sweet shift catalyst, the CO conversion was 95% in first step and 5% in the second step, which would make it possible to consider a shifting process with only one step.
- Achieving design specifications of the main streams has been very easy (CO_2 >99.6% and pure H_2 >99.995%).
- Auxiliary consumption is lower than estimated in design.
- Integration of operations and maintenance in the existing IGCC has been very easy.
- The rate of CO_2 captured is 91.7%.
- Cold gas efficiency is 89.5%.
- First estimation cost of avoided CO_2 is approximately 25–30 €/t.

Sotacarbo COHYGEN pilot plant

Although not an IGCC pilot plant, in order to develop and optimise an integrated process for a combined production of hydrogen and electrical energy through coal gasification, a pilot platform has been built at the Sotacarbo Research Centre in Carbonia, Italy (Maggio and others, 2009; Pettinau and others, 2010). The platform includes two different units: a 5 MWth pilot plant (with the main goal to optimise the gasification process) and a 200 kWth laboratory-scale plant (designed to develop and optimise the syngas treatment line for hydrogen production and power generation, with CO_2 separation). A CO_2 separation efficiency up to 85–90% has been obtained without solvent recirculation. In experimental tests, a hydrogen production of about 1.4–1.6 kg/h (depending on the primary fuel composition and the operating conditions) has been obtained from a portion of syngas corresponding to the gasification of 7 kg/h of coal. That is, for every kW of gasified coal, about 0.75 kW of hydrogen has been obtained. The experimental tests also showed a CO_2 absorption higher than 85%, which could be raised to 90–92% by operating at 0.25–0.30 MPa (Pettinau and others, 2010).

Zecomix pilot plant

www.zeroemission.enea.it/risorse-en-en/zecomix

In July 2005 the activities of the project ZECOMIX (Zero Emission Coal MIXed technology) started officially within the framework of a programme funded by the Italian University and Research Minister. The main aim of the project was to demonstrate, through a series of modelling and experimental activities, the feasibility of a new innovative process for 'zero emission' production of electricity and hydrogen from coal (Attanasi and others, 2011). The project is a mix of different processes, coal hydrogasification, clean-up of syngas, high temperature capture of H_2S and CO_2 using calcined dolomite, and combustion of hydrogen in a gas turbine, whose integration is the key factor to the high cycle performance and optimisation. It is shown schematically in Figure 11. Preliminary studies indicated very good results in terms of net electrical efficiency, with values close to 50%. The plant was designed to have a significant pilot plant size. Hence, the operative pressure has been set at atmospheric pressure and a coal mass flow about 50 kg/h. Plant construction started at the end of 2008 at the ENEA Cassaccia Research Centre, near Rome. The plant was in the commissioning phase by 2011 with hot tests on the carbonator due to begin in September 2011. The first calcination/carbonation tests with gasification integration are due to begin after April 2012.

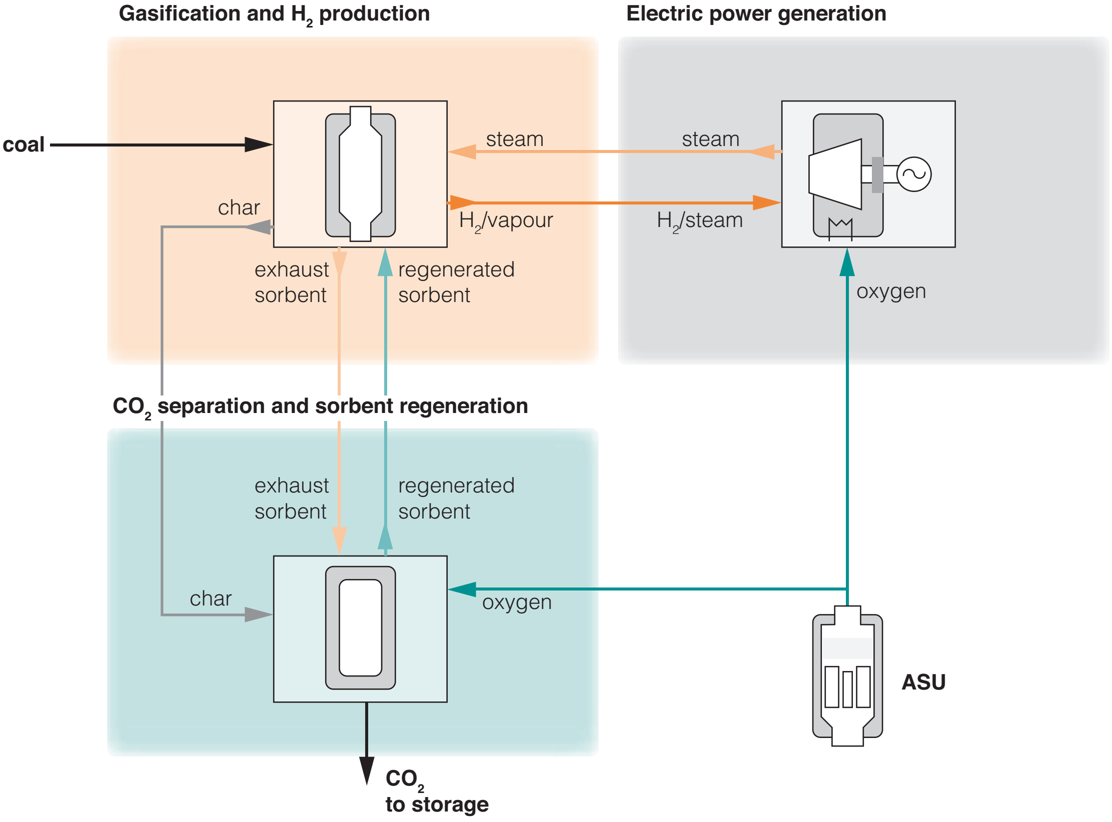


Figure 11 Schematic view of ZECOMIX process (Attanasi and others, 2011)

7.2 Planned and proposed plants

A good source of information on planned and proposed projects is the Global CCS Institute's projects database at http://www.globalccsinstitute.com/projects.

C.GEN Killingholme

www.cgenpower.com/en/projects_killingholme.html
In 2008, C.GEN acquired about 68 acres of land situated along the Humber estuary in the UK, next to the Humber Sea Terminal, and proposes to build the North Killingholme Power Project on this site.

The Project comprises:

- a 570 MWe power station configured to enable combustion of natural gas or hydrogen rich gas as fuel. The power station itself will include a gas turbine, a steam turbine and a heat recovery steam generator (HRSG). The HRSG generates high pressure steam that is used in the steam turbine plant to generate electricity;
- a solid fuel fired gasifier with associated infrastructure, including an air separation unit (ASU), a gas treatment system and equipment for the evacuation of CO_2 that has been removed from fuel prior to the combustion process.

The IGCC power station operating mode is designed to include a suitable solution for evacuating the CO_2 by an adequate transport and storage system. C.GEN considers that from an efficiency point of view, it is preferable that a CO_2 capture unit has to be included in the construction of the gasification plant equipment from the outset and not retrofitted at a later stage. This implies that the availability of a CO_2 evacuation solution is important for the development of a full IGCC plant with CO_2 capture. It is anticipated that the plant will begin commercial operation in 2015-16.

C.GEN's North Killingholme IGCC Project has been submitted on 9 May 2011 by the UK Government (Department of Energy and Climate Change) to the European Investment Bank for consideration in the next round of the EU's NER scheme.

C.GEN is also proposing to build an 800–900 MWe IGCC Power Plant in Vlissingen (Flushing) in the Netherlands. Again, commercial operation is planned for 2015. However, plans for a plant in Rotterdam have been abandoned due to the technical feasibility of the location, coupled with uncertainties regarding regulation and storage of CO_2 in the Netherlands.

Dongguan Taiyangzhou

The Dongguan Taiyangzhou Power Corporation in China is in the early phases of planning construction of a 750 MW net IGCC plant with CCS. The plant will be a new build IGCC power plant using coal as a feedstock and is expected to capture up to one Mt/y of carbon. The CO_2 would be transported in a pipeline and stored in near-depleted offshore oil and gas reservoirs about 100 km from the power plant. The plant would be operational for 20 years. Future moves to ramp-up the level of CO_2 capture depend on the cost and availability of storage sites (http://www.globalccsinstitute.com/projects/dongguan-taiyangzhou-igcc-ccs-project, *also* PEi, 2011a).

The Hatfield/Don Valley Power Project

www.2coenergy.com/don_valley_power_project.html

Powerfuel PLC began developing a £1 billion 900 MW IGCC plant with carbon capture near the Hatfield Colliery in Yorkshire, UK (Gibbons, 2008). It planned to finance and operate the first commercial, large-scale, coal-fired IGCC with CCS power plant in Europe. The project was to be developed in two phases: first the development of the syngas-ready power island then, after two or more years, to move production to a coal IGCC running on syngas with an associated carbon capture facility. The target date for generation was 2013. The European Commission set up a New Entrants Reserve (NER) in the Emissions Trading Scheme (www.ner300.com), from which 300 million allowances (corresponding to 300 million tonnes of CO_2 emissions or their cash equivalent which could be as much as €4.5 billion if each allowance is sold for €15) have been earmarked for the benefit of early projects in CCS and similarly innovative and currently non-commercial low carbon technologies (www.ccsnetwork.eu). The project, in partnership with National Grid, was awarded a €180 million grant in December 2009. It is anticipated that the final investment decision will be taken by mid-2013 and, after a construction period of a little over three years, the plant should be commissioned in 2016.

Hydrogen Energy California (HECA) project

http://hydrogenenergycalifornia.com/

The HECA project is a coal- and petcoke-based IGCC polygeneration plant in Kern County, CA, USA. More than 2.3 Mt/y of CO_2 will be captured from the coal gasification plant using Selexol™. The hydrogen produced at the gasification plant will be used locally to produce electricity from a 400 MW combined cycle block, as well as 1 Mt/y of urea and ammonia. Of the 400 MW generated by the power plant, 120 MW would be used within the industrial complex, with the remaining 280 MW being delivered to the grid at peak load. The CO_2 would be used for enhanced oil recovery at a nearby oil field. Over 90% of the CO_2 emitted at the industrial complex will be captured. The project is scheduled to commence commercial operations in 2017 (http://www.globalccsinstitute.com/projects/hydrogen-energy-california-project-heca).

Lianyungang

The Lianyungang Clean Energy Innovation Industrial Park in China aims to construct both a 1200 MW IGCC and a 1300 MW ultra-supercritical pulverised coal (PC) fired power plant. Heat integration is being pursued between the IGCC, ultra-supercritical PC and a solar heat collector to further improve the efficiency of the system. Up to 1 $MtCO_2$ would be recovered each year from the syngas and the ultra-supercritical PC flue gas. Captured CO_2 would be transported by pipeline to

Binhai, near Yancheng in the province of Jiangsu, for injection into saline formations or enhanced oil recovery. The pre-feasibility study has been completed and the feasibility study was expected to be completed by June 2011. The plant is anticipated to be operational by 2015, subject to government approvals. The Lianyungang Clean Energy Innovation Industrial Park has the objective of promoting industrial development based on clean energy to reduce the emissions of CO_2 and other greenhouse gases to the atmosphere (http://www.globalccsinstitute.com/projects/lianyungang-igcc-ccs-project , *also* PEi, 2011a).

Osaki CoolGen plant

www.osaki-coolgen.jp (In Japanese)
On 29 July 2009 the Electric Power Development Co Ltd and the Chugoku Electric Power Co Inc established a new company, Osaki CoolGen Corporation, through joint investment to undertake a large-scale demonstration test of oxygen-blown coal gasification combined cycle technology (oxygen-blown IGCC) and CO_2 separation and recovery technology. Osaki CoolGen Corporation will be responsible for the construction of the 170 MW demonstration test facility at the Osaki power station near Hiroshima. Construction of the IGCC plant is due to start in March 2013 with design and construction of the CO_2 separation and recovery beginning in 2017 leading to the IGCC plant being modified by 2021 (http://www.jpower.co.jp/english/news_release/news/news090729.pdf).

Polk power plant

Unit 1 of the Polk power plant owned by the Tampa Electric Company (TECO) in Florida, USA, is a 320 MW gross IGCC in service since 1996. A warm syngas clean-up process is to be installed and tested by RTI International (Gupta and others, 2010; also TECO, 2011a,b). RTI also proposed integrating this with carbon capture using aMDEA as a chemical solvent (‘conventional’ carbon capture technology). The aim is an 8000-hour operating programme capturing 300,000 t of CO2 per year with >90% CO2 capture. The schedule suggests commissioning and operation of the project between 2013 and 2015. The CO2 will be stored in a saline aquifer beneath the Polk power station. The size of the CO2 plume would not extend beyond the plant’s property limits (4000 acres or ~1600 hectares).

A case study published by the (US) National Coal Council (2011) seems to confuse matters by suggesting that the ‘proposed technology RTI intends to apply is the solid sorbent precombustion CO_2 capture from syngas. It will utilise warm gas clean-up with the sorbent. RTI is currently investigating Lithium Ortho-silicate ($LiSiO_4$), Lithium Magnesium, and MgO

sorbents.’ However, Table 2-1 in the same report lists the capture technology as amine based. It is likely that the report has confused the solid sorbent based warm gas clean-up for removal of COS and H_2S with the removal of CO_2. Certainly, in October 2011, Hornick and Gardner (2011) confirmed that after a shift reactor (sweet shift) and syngas cooling the carbon capture process would be based on aMDEA. The choice of aMDEA was due to its low capital cost and energy use, and the capture of up to 90% of available carbon in the syngas slipstream.

PurGen One

www.purgenone.com
PurGen One is a coal gasification project with carbon capture and storage located in Linden, New Jersey (http://www.globalccsinstitute.com/projects/purgen-one). The $5.2 billion project is being developed by SCS Energy LLC. The commercial-scale IGCC plant will have a nominal 500 MW of electric generating capacity, of which 90% of CO_2 emissions will be captured. The project will produce power as well as ammonia, urea, and sulphuric acid. 10 Mt/y of CO_2 transport capacity will be developed (with 3 Mt/y initially being captured and stored from the PurGen One plant itself) with storage off the New Jersey coast. A construction start in 2012 is anticipated.

South Heart Hydrogen Energy Project

Great Northern Power Development and Allied Syngas Corporation are proposing a 175 MW net lignite-based IGCC plant with about 90% capture of CO_2 in Stark County, ND, USA. The hydrogen produced will be used for power generation. Up to 2.1 Mt/y of CO_2 (90%) will be captured at the plant and used for enhanced oil recovery in the Williston Basin. Were construction to begin in July 2013, it is projected that operation would begin approximately four years later in July 2017. The 2010 estimated cost for the construction of the facility was $2.2 billion (http://www.globalccsinstitute.com/projects/quintana-south-heart-project; http://plainsjustice.org/files/12-13-10%20hydrogen%20plant%20letter%20of%20intent.pdf).

Taylorville Energy Center

http://cleancoalillinois.com/tec.html

Taylorville Energy Center is planned to be a 602 MW net IGCC power plant (http://www.globalccsinstitute.com/projects/taylorville-energy-center). It will convert Illinois coal into clean syngas and is seeking to capture more than 50% of the CO_2 that otherwise would be emitted into the atmosphere. Approximately 3 Mt/y of CO_2 will be produced and will be transported via pipeline. Storage options include enhanced oil recovery (EOR) or deep saline formations. US$18 million in Front End Engineering and Design (FEED) study funding has been granted from the Illinois Department of Commerce and Economic Opportunity. The projected commercial operation date for the project is in 2016. However, the proposal by Tenaska Energy to build the $3.5 billion plant did not pass the Illinois state Senate in October 2011. It is possible that it may be considered again later in the spring of 2012 (Power Engineering, 2011).

Teesside CCS Project

http://www.progressive-energy.com/

The Teesside CCS Project (Eston Grange) is a proposed new build 850 MW IGCC power plant using bituminous coal as a feedstock. Capture of around 5 Mt/y of CO_2 from a 400 MW slipstream through pre-combustion capture technology is planned. The CO_2 will be transported via pipeline for storage in offshore deep saline formations. Financing round is currently under way and additional investors are being sought. One of the original partners in the project, Centrica, has divested its share back to Progressive Energy due to issues relating to investment risk. The project is scheduled to reach commercial operation in 2016 (http://www.globalccsinstitute.com/projects/eston-grange-ccs-plant). The Teesside CCS Project has been submitted by the UK Department of Energy and Climate Change to the European Commission under the NER300 Process.

The Texas Clean Energy Project

www.texascleanenergyproject.com

The Texas Clean Energy Project (TCEP) was awarded $450 million under the US DOE Clean Coal Power Initiative (CCPI) round three programme on 29 January 2010 (Ciferno and others, 2011). The TCEP, owned by Summit Texas Clean Energy LLC, will be a greenfield IGCC polygeneration facility with fully integrated CO_2 capture to be located in Penwell, Ector County, Texas. The TCEP will use subbituminous coal to produce electricity for export to the grid and other high value marketable products, such as sulphuric acid, urea, and CO_2. The IGCC facility will deploy Siemens commercial gasification and power block technologies, including Siemens combustion and steam turbine-generator sets. The facility will use WGS and Linde Rectisol® CO_2 scrubber technology to capture about 90% of the CO_2 produced from the 400 MW (gross) facility. The CO_2 will be compressed and transported by existing regional pipelines to oilfields in the west Texas Permian Basin for beneficial use in enhanced oil recovery (EOR) operations. The total project value is $1,726,628,229.

Some further information can be found in a report by Gas Turbine World (2011) of a conference presentation by Barry Cunningham, Summit managing director of project development. The plant is scheduled to start construction in 2012 and enter service in 2015. Urea production for agricultural fertilisers is expected to be the biggest component of the plant's revenue stream at 46%. The plant will yield 190 MW net for electric power sales to the grid. An unidentified conference participant was reported as commenting that the process 'cannibalises about 50% of the electricity' produced.

Wandoan Power Project

In Australia, GE Energy and Stanwell Corporation, in an alliance with Xstrata Coal Queensland have produced a pre-feasibility study which examined a 340 MW net IGCC power plant with carbon dioxide capture (Wandoan Power Consortium, 2011). Up to 2.5 Mt/y of CO_2 could be captured at the plant. Regional storage capacity in the Surat Basin is proposed. The pre-feasibility study indicated a target date for start-up around 2017-18. The project was selected for consideration of funding support by the Commonwealth of Australia's CCS Flagship Programme. In June 2011, the federal government announced that it will continue to progress other large-scale Australian CCS projects, including the Wandoan project in Queensland. Wandoan Power's pre-feasibility study financial modelling indicates that if the project is developed with a grant funding contribution of AU$ 1800 million applied to the construction phase then the project's LCOE is 192 AU$/MWh in current dollars.

7.3 Abandoned projects

It was noted above in Section 7.2 that C.GEN has abandoned plans for a plant in Rotterdam due to the technical feasibility of the location, coupled with uncertainties regarding regulation and storage of CO_2 in the Netherlands. Other plans for IGCC plants have also been abandoned.

In early 2006, RWE Power announced a plan to build a commercial lignite-based IGCC plant with carbon capture (Wolf, 2006; Wolf and others, 2007). Commissioning was planned for 2014. Further details were given by Renzenbrink and others (2007, 2009a,b; Keller and Scholz, 2010). In the concept development, sour shift and capture by the Rectisol® process were envisaged. The gross efficiency of the overall plant was to be 48.5% (LHV) and a net efficiency of 34% (LHV). The overall carbon capture rate was expected to be about 92%. But, by 2010, things started to become less certain, the expected German CCS law was not adopted in 2009 (Renzenbrink and others, 2010). The initial approval by policy makers had turned into outright refusal for storage resulting in RWE suspending any further implementation of the project. Eventually, as announced on the RWE website (2011), the implementation of the IGCC-CCS project required that the German Carbon Storage Law (KSpG) be passed and that policy makers promote acceptance of the CCS technology. Without this framework, the exploration of suitable storage sites was not possible. Without a CO_2 storage facility, the route for the pipeline could not be planned. Without the pipeline and storage facility, on the other hand, the construction of a power plant designed for CCS was neither viable nor sensible from the perspective of climate protection. Thus, RWE deferred the first steps necessary to implement the IGCC project in Hürth and put the brake on the engineering activities for the power plant. RWE banks on the speedy creation of a legal framework and the improvement of the acceptance situation in particular as regards CO_2 storage and transport.

In the UK, E.ON announced a large-scale demonstration IGCC plant to be located near Killingholme on the east coast of England (Irons, 2006; Periselneris and others, 2007). It was recognised that the cost of IGCC with CCS would be high, therefore it was important to support the first project adequately as well as forming a framework to support future projects. However, the UK Government's decision to fund post-combustion capture only, led to work on Killingholme being stopped. However as noted in Section 7.2 above, the project has been revived by C.Gen.

The FutureGen plant was envisaged as a means of establishing the technical, economic, and environmental viability of 'zero-emission' coal plants by 2015; thus, creating the option for multiple commercial deployments by 2020 (Mudd, 2007). It would capture >90% CO_2 with potential for ~100%. It was to have been a gasification-based plant generating electricity and producing hydrogen. It is now FutureGen 2.0 (http://www.futuregenalliance.org/futuregen-2-0-project/). In co-operation with the US Department of Energy, the FutureGen 2.0 project partners will upgrade a power plant in Meredosia, IL, with oxy-combustion technology to capture approximately 1.3 $MtCO_2$ each year – more than 90% of the plant's carbon emissions.

The ZeroGen project (www.zerogen.com.au) was to have been a staged commercialisation programme involving the deployment of IGCC with CCS for low carbon emission power generation. The technology was to be deployed at demonstration scale (approximately 130 MW gross) by 2012, and at large scale (approximately 400–450 MW gross) by 2017. The demonstration-scale IGCC facility was planned to be located adjacent to the Stanwell Corporation's coal-fired thermal generation station near Rockhampton in Central Queensland, Australia, with the CO_2 storage site located approximately 220 kilometres west of the IGCC facility. The primary objective of the demonstration programme was to validate IGCC with the application of CO_2 capture and sequestration in geological formations for a coal-based power generation facility (Oettinger and others, 2008; Grieg, 2009). The Queensland Government provided $102.5 million funding for the feasibility study and earmarked $300 million for the project subject to the outcome of the feasibility study and business case (QGMJ, 2008). A pre-feasibility report was submitted and a precis of the approaches taken to managing risk and uncertainty was given by Garnett and others (2011). In December 2010, the Queensland Government announced that it would not pursue the proposal to fund the project on the basis that the early research had shown that it was not viable at this time on a commercial scale (Queensland Government, 2010).

7.4 Comments

In the context of the planning of the Zerogen project, one argument for the need for such a plant was that few, if any, fully integrated IGCC with CCS demonstrations have been completed and so there are no benchmarks for performance, cost and time (Grieg, 2009). There remains a need for a demonstration of an IGCC plant with integrated CO_2. Ways of capturing CO_2 are already known, but whether they can be incorporated into a coal gasification plant producing electric power rather than hydrogen or chemicals needs to be demonstrated.

8 Conclusions

Thambimuthu (2008) has pointed out that, although combustion-based carbon dioxide capture processes such as post-combustion capture and oxyfuel combustion have a big advantage in that they can cut carbon from many existing power plants, they are restricted mainly to the production of low carbon heat and electricity, capturing on average 85–95% CO_2. On the other hand, coal gasification, where CO_2 is captured ahead of combustion, offers wider possibilities for the production of heat, electricity and hydrogen along with carbon-free to carbon-neutral chemicals and liquid transportation fuels.

CO_2 capture in gasification plants has been proven technology for years but not in an IGCC context. The objective has been to obtain chemical products rather than to produce electric power. These plants use physical solvents to capture the CO_2 but, if used in IGCC plants, there is the need to cool the gas to allow CO_2 capture followed by heating it up again for firing the IGCC gas turbine. This decreases the plant thermal efficiency and thus increases the overall costs. But, they do have advantages. As Higman (2010) has pointed out, despite physical solvents having a higher capital cost than amine washes, the lower steam consumption and superior selectivity are probably the principal reasons behind what is ultimately an economic decision. The fact that physical washes can deliver part of the CO_2 at an elevated pressure, thus reducing CO_2 compression costs, also contributes to their attractiveness in this service.

One way of avoiding gas cooling and heating would be to use solid sorbent to capture CO_2 and, as Siriwardane and others (2005b) have noted, CO_2 removal at warm gas temperatures (200–350°C) is the most energy efficient for IGCC systems to prevent loss of thermal efficiency due to cooling of the gas. There has been a considerable amount of research into sorbents capable of being used in IGCC plants, and incorporation of sorbents into the WGS reactor looks promising even though any H_2S captured would have to be removed from the CO_2 prior to storage. It is not yet clear how separate H_2S and CO_2 streams could be produced if they have been captured together. Also, it is not clear how much make-up sorbent would be needed in the SEWGS. It would probably be less than that needed if the sorbent is located in the gasifier but it could possibly be of the same order. If there are large quantities of sorbent to be disposed of, then integration with cement production would probably be necessary but this could limit IGCC plants with SEWGS CO_2 capture to locations close to cement production. Even so, there is still no commercially-available adsorption process for pre-combustion capture.

Although membrane removal of CO_2 from flue gas is difficult due to low driving force and the presence of trace contaminants which are molecularly very similar to CO_2, such as SO_2, separation of CO_2 from syngas is more advantageous since it is already at high pressure and possesses a higher concentration of CO_2 after the WGS. In a manner similar to SEWGS, combining shift catalysis with membrane separation in membrane reactors could reduce the number of process stages and significantly improve process efficiencies, enable operation at higher temperatures, and reduce steam consumption. However, there is still scope for improving the reliability and durability of membranes in a coal syngas environment. Much of the R&D emphasis has been on H_2 selective membranes and there is scope for further research into CO_2 selective membranes.

The techno-economic studies that have been carried out are mainly best guesses based on likely costs and also on the predicted performance of technologies that are yet to be fully developed such as hydrogen separation membrane reactors. One problem is that there is no IGCC plant without CO_2 capture that can be used as a reference power plant case because these types of plants have not been constructed in the last decade and the four existing IGCC power plants are best described as first-of-a-kind demonstration plants. No reliable cost data therefore exist. It remains the case that, when comparing pre-combustion capture with other technologies such as post-combustion capture and oxyfuel combustion, the investment costs, COE, and net efficiencies of the different CO_2 capture technologies are still found to be comparable. In economic terms no clear winner has yet emerged.

Few, if any, fully integrated IGCC with CCS demonstrations have been completed and so there are no benchmarks for performance, cost and time. There remains a need for a demonstration of an IGCC plant with integrated CO_2 capture. Ways of capturing CO_2 are already known, but whether they can be incorporated into a coal gasification plant producing electric power rather than hydrogen or chemicals needs to be demonstrated.

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