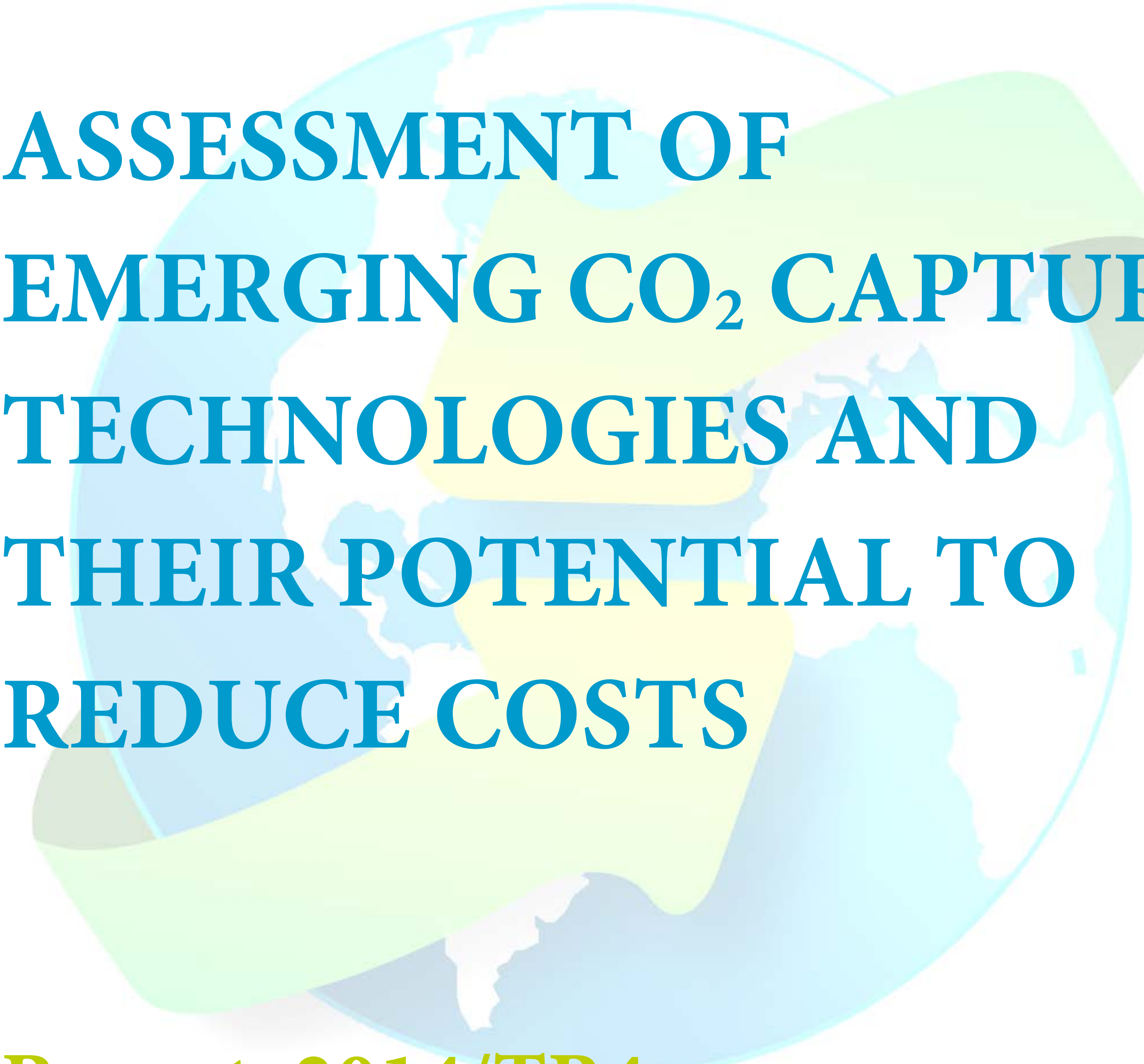

ASSESSMENT OF EMERGING CO_2 CAPTURE TECHNOLOGIES AND THEIR POTENTIAL TO REDUCE COSTS

Report: 2014/TR4

December 2014

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Assessment of Emerging CO_2 Capture Technologies and their Potential to Reduce Costs

Executive Summary

Introduction

This Technical Review gives an interim overview of research and development aimed at improving and reducing the cost of commercial scale carbon dioxide capture in the power and process industries. It considers technologies principally applicable in post-combustion capture, pre-combustion capture, oxy-combustion capture and finally systems with circulating solids; in that order, which is more or less in line with the current maturity of each approach. It then goes on to consider applications in iron and steel and cement production and oil refining. IEAGHG's normal practice is for its reports to be sent to external reviewers and for the reviewers' comments to be taken into account prior to publication. This Technical Review is an interim report which has not yet gone through this process. An IEAGHG Report which has been subject to external review will be published in due course.

The report describes the general status of research and development and the main organisations carrying it out. It also examines the potential impact which each approach could have on the energy consumption and cost of electricity when capture is applied. It does this where possible on the basis of the thermodynamic fundamentals of the process and comparison with benchmark estimates for the established capture processes. Many cost reduction claims are found in the literature but these have been assessed critically as they sometimes give a misleading view of the magnitude of potential improvements. For purposes of comparison the percentage increase in Levelised Cost of Electricity (LCOE) is used as the principal cost comparator. This relates closely to the cost of CO_2 abatement which can be calculated directly if also the efficiencies of baseline and capture plants and the fraction of CO_2 captured are known. Where precise figures are not available a descriptive statement of the potential for cost reduction is given. Working on a percentage basis eliminates most of the variations in estimates which can arise from different assumptions regarding discount rate, project lifetime, region and currency.

Figure 1 below illustrates the estimated percentage increase in LCOE over a baseline supercritical steam coal-fired power plant when current post-, oxy- and pre-combustion capture technologies are added. This data has been extracted from the detailed studies performed by the US National Energy Technology Laboratory (NETL) and includes an adjustment so that the comparison is on the basis of plants of equal gross thermal energy input. The percentage increases of 80-100% in LCOE are the target which must be bettered by alternative capture technologies.

The costs in Figure 1 are based on one set of assumptions for each capture technology and the differences in cost increase are not large enough to indicate a strong preference for one class of technology over the others. The increase in LCOE for adding pre-combustion capture to an IGCC plant is lower than the costs of adding post and oxy-combustion capture to pulverised coal plants but the LCOE of an IGCC without capture is higher than the LCOE of the baseline pulverised coal plant without capture, which eliminates the cost advantage of pre-combustion capture.

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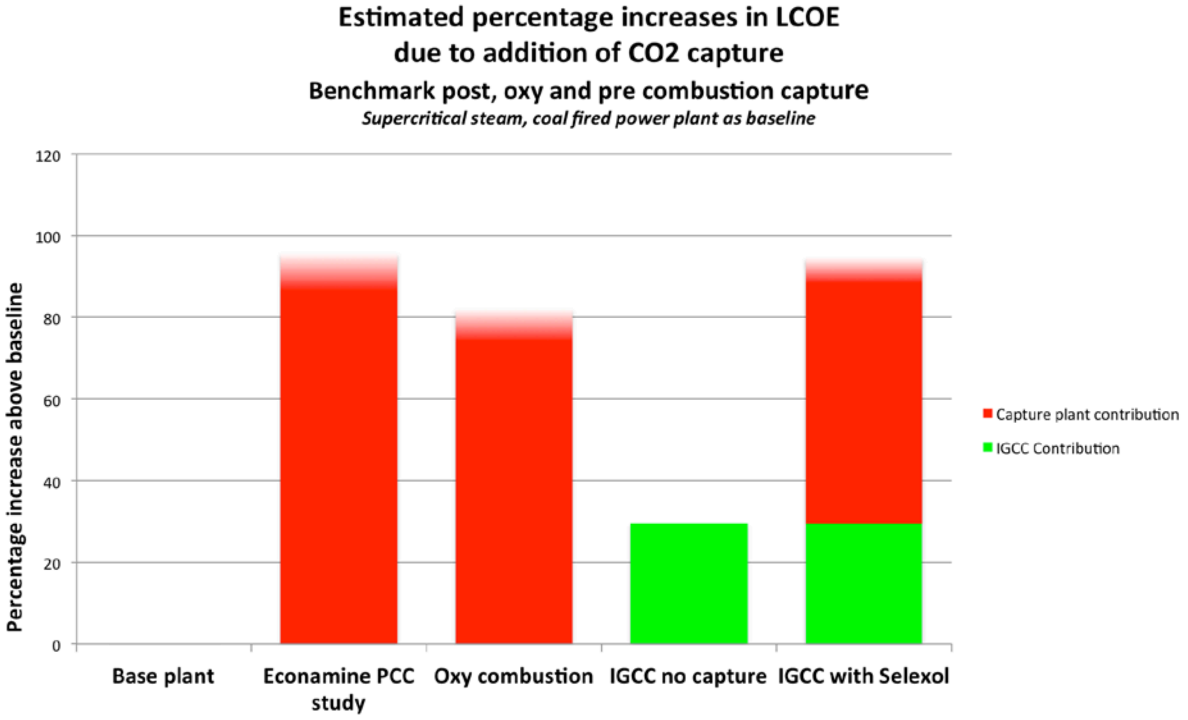


Figure 1 LCOE increases due to CO_2 capture

The state of development of emerging technologies is assessed on a nine point numeric scale of Technology Readiness Level (TRL) based on the descriptive definitions proposed by the Electric Power Research Institute (EPRI). These are summarised in Table 1.

Table 1 Technology Readiness Level (TRL)

Demonstration	9	Normal commercial service
	8	Commercial demonstration, full scale deployment in final form
	7	Sub-scale demonstration, fully functional prototype
Development	6	Fully integrated pilot tested in a relevant environment
	5	Sub-system validation in a relevant environment
	4	System validation in a laboratory environment
Research	3	Proof-of-concept tests, component level
	2	Formulation of the application
	1	Basic principles, observed, initial concept

In this report the TRL is assessed for the main CO_2 capture technologies under development and there is a focus on those which are already at levels 4, 5 and 6.

Many of the technologies have potential to be used in more than one of the four main types of capture processes and in specific industries. To avoid repetition, the first time a technology is discussed its key cost reduction and thermodynamic characteristics will be explained. The reader is referred back to this first description if the technology is discussed in the context of any of the other main capture routes later in the report.

Post-combustion capture

The study identified about 16 technological approaches to improve post-combustion capture. These range over the full range of maturities and mostly they offer marginal reductions in LCOE and energy consumption. There are also novel approaches which on analysis may not offer either reductions in cost or energy consumption.

TRLs and LCOE reduction prospects for these technologies are assessed in Table 2. Technologies at TRL 4-6 are highlighted in green and those considered to have good prospects for cost reduction are highlighted in yellow for smaller, green for more significant and red for high potential. Improvements to conventional solvents are at high technology readiness level as existing solvent formulations can usually be changed out very easily. The potential for cost reductions is, however, relatively small. There is also scope for incremental improvements through a greater degree of heat integration and the main report indicates broadly, in terms of efficiency reduction, what this potential is.

Precipitating and biphasic liquid solvents are identified as having interesting potential for cost reduction but are at a relatively early stage of development. The use of membrane separation appears to have considerable potential to reduce cost, although this is heavily dependent on the cost per unit area of membrane surface. Much of the cost advantage would come from the much lower specific energy consumption in membrane processes arranged in an innovative way to use combustion air as a sweep gas. The study has also identified that this innovative process arrangement might be applied to other combinations of separation technologies.

Table 2 TRLs and LCOE reduction prospects –Post-combustion capture

Technology	TRL	Prospects to reduce the LCOE increase for capture
Benchmark proprietary mono-ethanolamine (MEA) process	9	LCOE increase expected to be about 100% of baseline
Improved conventional solvents	6-8	Incremental reductions possible
Encapsulated solvents	1	Potential still to be proven
Precipitating solvents	4-5	5-10%
Biphasic solvents	4	16%
Ionic liquids	1	No viable process yet
Polymeric membranes	6 (fast development possible)	30%
Polymeric membrane/cryogenic separation hybrid	6 (fast development possible)	Similar or better than polymeric membrane alone
Room temperature ionic liquid (RTIL) membranes	2	Could be similar or better than polymeric membranes
Enzyme catalysed adsorption	1	7% Incremental reduction due to reduced absorber size
Algae based capture	1	Unlikely in mid-term future
Electrochemically mediated absorption	1	High electrical energy consumption makes reduction unlikely
Cryogenic capture	3 (fast development possible)	Moderate reduction possible if favourable assumptions are valid
Supersonic inertial capture	1	Too early to validate
Vacuum pressure swing adsorption (VPSA)	3	Relatively high energy requirement makes significant reduction unlikely
Temperature swing adsorption (TSA) with thermal regeneration	1	Uncertain
TSA with electric regeneration	1	Likely much higher

Energy requirements – Post-combustion capture

The report looks in some detail at the energy requirement for the capture of CO_2 and how this is coupled to the LCOE. In this report, estimates of the electrical equivalent energy consumption per tonne of CO_2 abated have been derived from information about process performance published in the literature.

The theoretical separation energy for post combustion capture is very low compared to the requirements of today's typical processes, as shown in Figure 2, indicating that there is considerable scope for reduction. However, practical processes are unlikely to be able to approach this energy consumption. What the chart does not show is that significant work could be obtained by exploiting the loss of exergy, which occurs because power production thermodynamic cycles are unable to use the full temperatures of combustion of fuel. Some of the emerging capture process are able to tap some of this energy, thus potentially reducing the parasitic energy load on the power plants in which they might be incorporated.

In addition to separation, the captured CO_2 has to be compressed for transport and storage. In a typical pulverised coal fired power generation process approximately 6% of the gross power is required for compression from atmospheric pressure to 150bar if 90% of the CO_2 is captured. This is shown by the difference between the blue and red lines in Figure 2. Some extra auxiliary power is also typically required by the capture process itself, for fans, pumps etc. There are significant multiplicative effects because energy inefficient processes result in consumption of more fuel and hence there is more CO_2 to capture and compress for the same net output of electricity. Figure 2 shows that the energy for compression of CO_2 (the difference between the blue and red lines) becomes an increasing proportion as the energy consumption of the capture process rises.

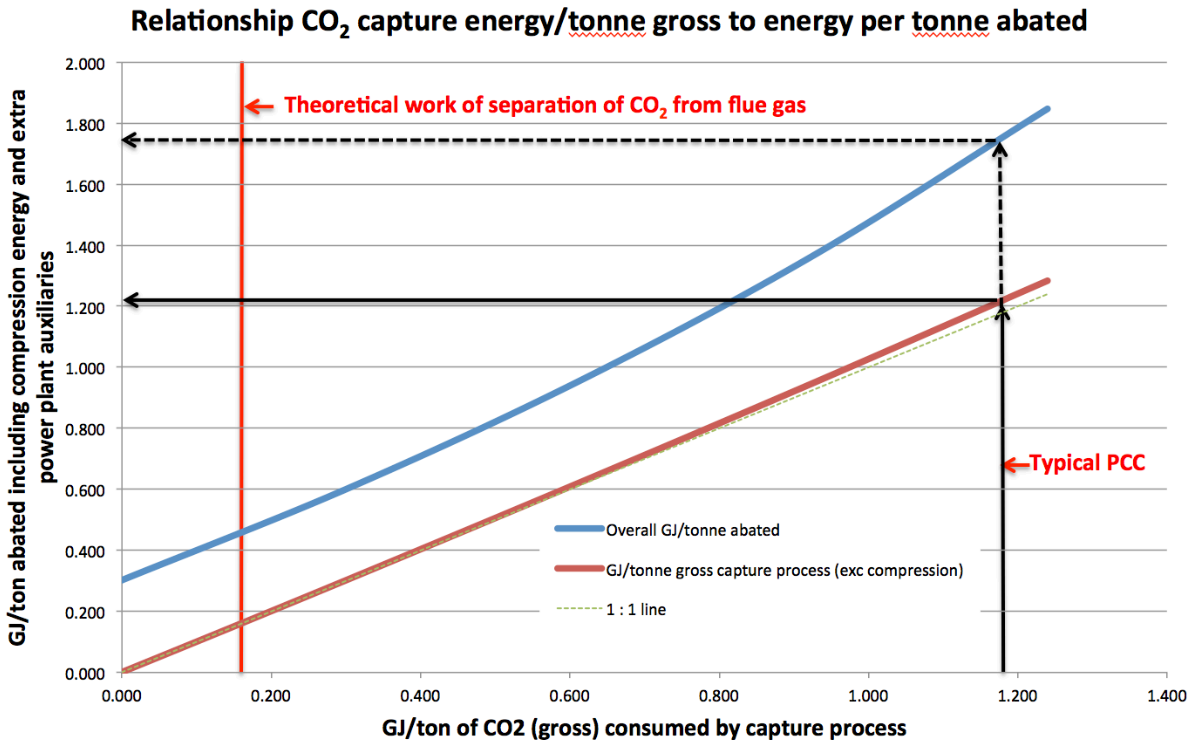


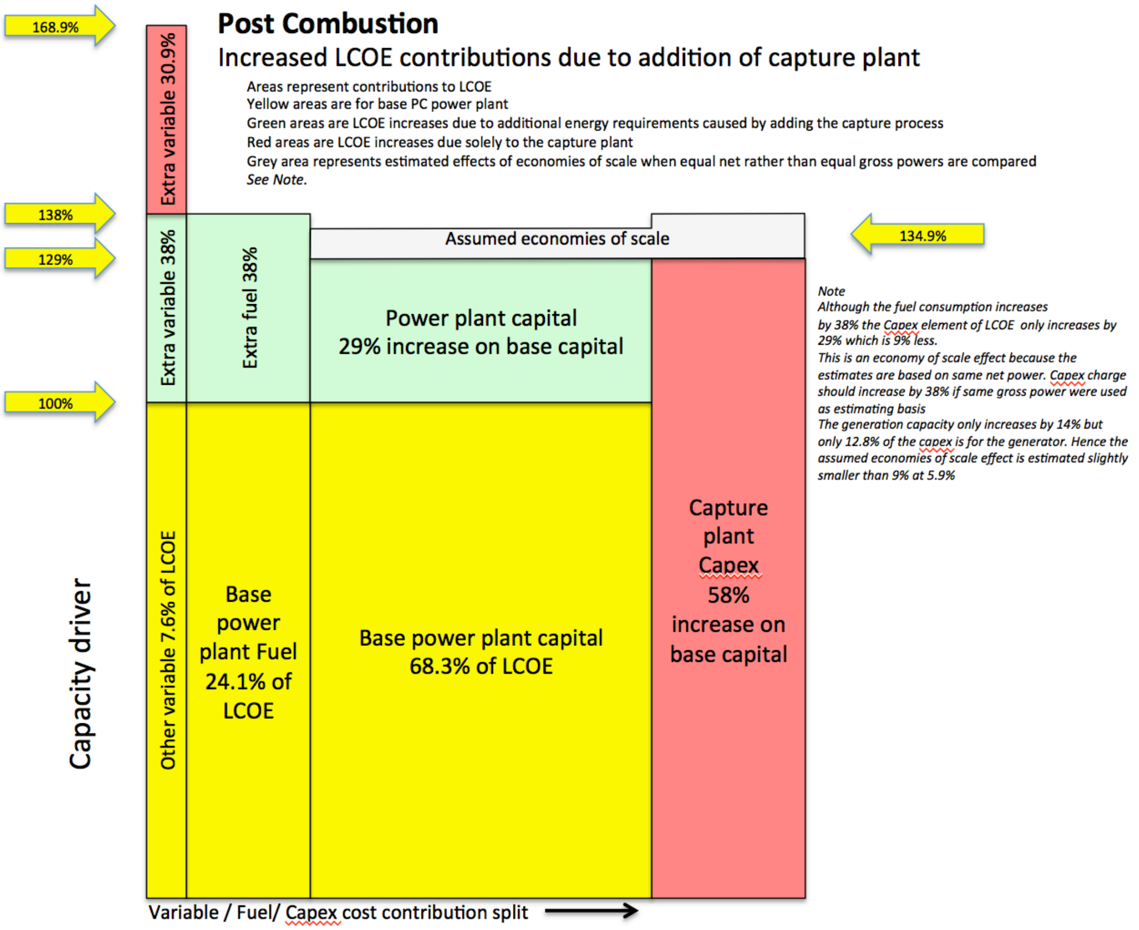
Figure 2 Relationship between capture energy per ton CO_2 gross and abated

In selecting the most promising areas for research and development, sound assessment of the energy reduction potential is thus essential. This is not only because of the implications for cost, energy security and environmental impacts of higher fuel consumption but also because there are significant knock on effects on capital costs and other operating costs. More detailed information on specific energy consumptions is in the main body of the report.

Cost drivers – Post-combustion capture

For comparison, either the increase in the levelised cost of electricity (LCOE) per unit of energy or the cost per unit of CO_2 abated should be used. This summary focusses on LCOE.

There are two main drivers for the increased LCOE of post-combustion capture plants. Analysis of the costs of a baseline post-combustion capture plant reveals that about 40% of the increase is due to the effects of the energy consumption. This requires extra fuel, increased investment in the power plant to generate the extra heat and power needed and significant contributions to both fixed and variable costs. The other about 60% of the increase in LCOE is simply attributable directly to the cost of the capture plant. The contributions to the LCOE increase are illustrated in Figure 3 in which the areas are proportional to the LCOE contribution.



Post Combustion

Increased LCOE contributions due to addition of capture plant

Areas represent contributions to LCOE
Yellow areas are for base PC power plant
Green areas are LCOE increases due to additional energy requirements caused by adding the capture process
Red areas are LCOE increases due solely to the capture plant
Grey area represents estimated effects of economies of scale when equal net rather than equal gross powers are compared
See Note.

Note
Although the fuel consumption increases by 38% the Capex element of LCOE only increases by 29% which is 9% less.
This is an economy of scale effect because the estimates are based on same net power. Capex charge should increase by 38% if same gross power were used as estimating basis
The generation capacity only increases by 14% but only 12.8% of the capex is for the generator. Hence the assumed economies of scale effect is estimated slightly smaller than 9% at 5.9%

Figure 3 Post-combustion - contributions to LCOE increase

Part of the LCOE increase due to the capital cost of the capture plant is due to the capture plant having to be bigger to handle the increased emissions caused by the parasitic energy consumption. This element is thus also driven by the size of the parasitic energy consumption of the capture plant. Reductions in fuel consumption are thus almost as important as reductions in the capital cost of capture equipment and any process in which only one of these is reduced needs careful analysis, as claims that this would lead to overall cost reduction on the basis of reductions in one of these drivers will not be valid if there is a significant increase in the other. Most of the technologies are targeting the energy consumption element even though the capital cost is the bigger driver.

Technologies which might target the capital cost driver for post combustion capture are enzymatic catalysis and membranes. The cost per m^2 of membranes is highly uncertain and cost estimates are driven by the unit price. Membrane based processes seem viable at seemingly conservative prices, so that research is worthwhile both to improve separation performance but also to reduce unit cost.

There may be scope for reduction in capital costs through innovation in equipment design or construction methods. This type of technology improvement tends not to be covered in the CCS literature and is probably applicable to wider industry and a literature search with a different focus would be required to identify these. For example, a cheaper method for construction of large concrete structures may potentially be a fruitful area of research, as the absorber column for conventional solvents is a major cost element.

The benchmark for the yellow area in Figure 3 is a supercritical coal-fired power plant as evaluated by NETL [NETL 2012]. The LCOE comparison of plants with and without capture in this report is on the basis of plants with equal fuel feed rates. If the comparison was on the basis of equal net power output, as in the source reference for post combustion capture, the cost increases would be lower because of economy of scale effects, as shown by the grey area in Figure 3.

Pre-combustion capture

As for post-combustion capture, each technology has been assessed and the TRLs and cost reduction potentials are indicated in Table 3 below.

Capture technologies have to be closely integrated into pre-combustion power plants making large scale demonstration of complete systems more difficult. However, the equipment for the heat and power integration is generally based on well-established technology, so there may be less necessity to demonstrate complete systems before proceeding to commercial scale. Two technologies; hydrogen separation membranes and sorption enhanced water gas shift, offer substantial cost reductions but still require significant development. Low temperature separation also offers considerable potential but is as yet at a very early stage. Integration of solid oxide fuel cells into IGCC has the potential to perform capture at almost no additional cost. However, although the technology is well into the development stage, there are significant scale up hurdles.

Table 3 TRLs and LCOE reduction prospects - Pre-combustion capture

Technology	TRL	Prospects to reduce the LCOE increase for capture
Benchmark IGCCs with Selexol	9	LCOE increase* expected to be about 100 -130% of baseline
Warm gas clean-up (can be used in combination with capture)	8 (if start-up successful)	3% reduction
Hydrogen separation membrane (including warm gas clean-up)	5 (if tests successful)	25% reduction
Sorption enhanced water gas shift (SEWGS)	5	30% reduction
Low temperature separation	2	30% reduction
Low temperature separation with CO_2 recycle	2 (rapid development possible)	50% reduction
Integrated gasification fuel cell (IGFC)	4-6	70-95% reduction#

** Lower figure for GE gasifier, higher for Shell gasifier.*

 # Higher figure assumes wide selection of technology advances

Energy requirements – Pre-combustion capture

The efficiency losses in pre-combustion processes are more complex to analyse than in post-combustion processes because some of the losses are incremental in systems intrinsic to the main process. In post-combustion capture there is a clear single separation task and usually a simple compression for the captured CO_2. Pre-combustion capture involves chemical conversion as well as separation and other knock-on effects. A good example is the loss of efficiency in the gas turbine when this is converted to run on hydrogen instead of syngas. The literature tends thus to report in terms of overall efficiency reduction with less specific information available about work required for separation. There are several benchmarks for IGCC with capture using Selexol; the differences reflect the performance of different types of gasifiers.

Cost drivers – Pre-combustion capture

The additional cost of equipment for pre-combustion capture processes is somewhat lower than for post-combustion. However the LCOE contributions of capital and non-fuel variable elements is higher for a baseline IGCC (integrated gasification combined cycle) plant without capture than the conventional pulverised coal (PC) plant without capture. The split of contributions to LCOE is illustrated in Figure 4. The area of the blocks represents the size of the contribution.

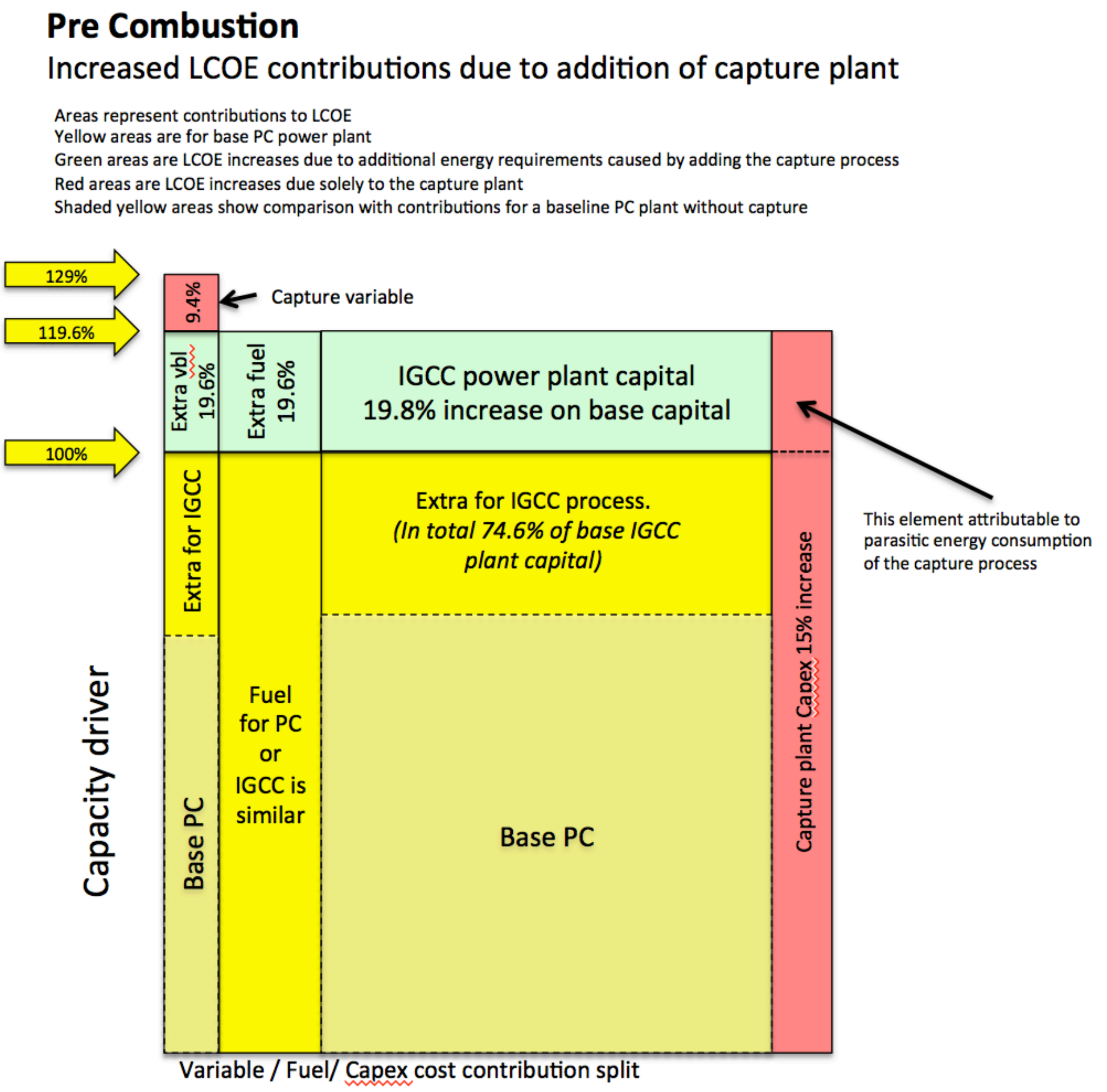


Figure 4 Pre-combustion – contributions to LCOE increase

Figure 4 illustrates that the main driver for the increased LCOE, when capture is applied, is the energy loss which drives about two thirds of the increase. Thus unlike post-combustion capture, where the capital cost of capture equipment is a significant target for cost reduction, for pre-combustion capture process efficiency is more important. Indeed, more expensive processes are certainly in the frame if these lead to substantial improvements in efficiency.

The efficiency of baseline IGCC plants varies by about 3% depending on the type of gasifier selected. The baseline here is taken from the NETL analysis for a General Electric (GE) gasifier based IGCC with capture [NETL 2010]. This has the lowest efficiency but has lowest LCOE with capture. The baseline PC is as for the earlier diagram (Figure 3). There is no 'economy of scale' grey area in this diagram because the fuel feed rate and net power output of IGCC plants are fixed by the size of the gas turbines and they cannot be varied, unlike pulverised coal plants.

Oxy-combustion

Most coal-based oxy-combustion developments can be considered as adaptations of mainstream power plants in which conventional combustion equipment is used with oxygen instead of air and there is a recycle of flue gases to mitigate temperatures in burners and furnaces. There are also developments of novel combustion turbine systems employing circulation of water and/or CO_2.

Within the mainstream development there are three key areas: the furnace and associated recycle systems, the air separation unit (ASU) and the CO_2 processing unit (CPU), which cleans up and pressurises the CO_2 for transport.

Research and development is taking place in all of these areas and the TRL assessments are shown in the table below. This identifies which parts of the system are targeted. There is some work on alternative oxy-combustion systems which are also described in the report.

Table 4 TRLs and LCOE reduction prospects – Oxy-combustion

Technology	Applicable capture process element	TRL	Prospects to reduce the LCOE increase for capture
Benchmark oxy-combustion	Oxy	7	80% increase over base LCOE
Furnace and boiler	Boiler	9	Small reductions
O_2 production - ASU development	ASU	9	22% reduction for target 40% reduction in ASU power
O_2 production – Direct drive	ASU	8	3% if power losses reduced by 5%
O_2 production – Ion transport membrane (ITM)	ASU	7	24% reduction claimed
O_2 production - Oxygen transport membrane (OTM)	ASU	4	Too early to tell
O_2 production – Ceramic autothermal recovery system - CARS	ASU	4	Too early to tell
CO_2 process unit – warm gas clean up	CPU	6-7	Minor
CO_2 process unit - Inert removal	CPU	8	Minor
CO_2 process unit – Recovery from vent	CPU	7	2-3% reduction if O_2 and CO_2 recovered.
CES's oxyfuel turbine cycle	Full system	5	Too early to tell
Other oxyfuel turbine cycles	Full system	2	Too early to tell

The assessment of percentage reductions in the table is based on analysis of performance figures and a simple model of how changes in the energy consumptions of ASU, CPU and the main plant auxiliaries interact with the main elements of the LCOE increase. Significant reductions in the LCOE increase are targeted by cryogenic ASU development. This gain is matched by the more revolutionary ion transport membrane process being developed by Air Products.

Potentially competitive alternative technologies which employ completely different thermodynamic cycles are being developed by CES and NET Power. Development work is currently focussing on gas fired power plants but they could also potentially use syngas from coal gasification.

Energy requirements – Oxy-combustion

Most information on energy consumption concerns the power requirement for the ASU. Reductions, where figures are available, have been translated into plant efficiency changes. At this stage no assessments have been included for novel oxy-combustion processes. More independent work will be required on these to establish true potential. The major industrial gas companies all have on-going development programs to reduce the cost of producing oxygen on a very large scale, which target gasification/gas-to-liquids (GTL), steel as well as oxy-combustion requirements, which differ in purity needs. A surprising finding [NETL 2008] is that a coal-fired oxy-combustion power plant using the ITM process would have similar efficiency to its cryogenic counterpart. The claimed 24% reduction in additional LCOE thus needs further investigation.

Cost drivers – Oxy-combustion

The main contributors to LCOE are illustrated in Figure 5 below. Again, the areas of the blocks illustrate relative contributions. The estimated LCOE increase for application of oxy-combustion is somewhat less than for solvent based post-combustion capture according to the reference used in this study but the figures should be taken as only a rough indication.

The parasitic energy is a slightly bigger driver than capital for the capture process in conventional coal-fired oxy-combustion systems. This is reflected in the emphasis which is placed on reducing the specific energy requirement for producing oxygen, which is the main consumer of extra energy. Note that the baseline PC plant here is slightly different, being that from the NETL study on oxy-fuel processes [NETL 2008].

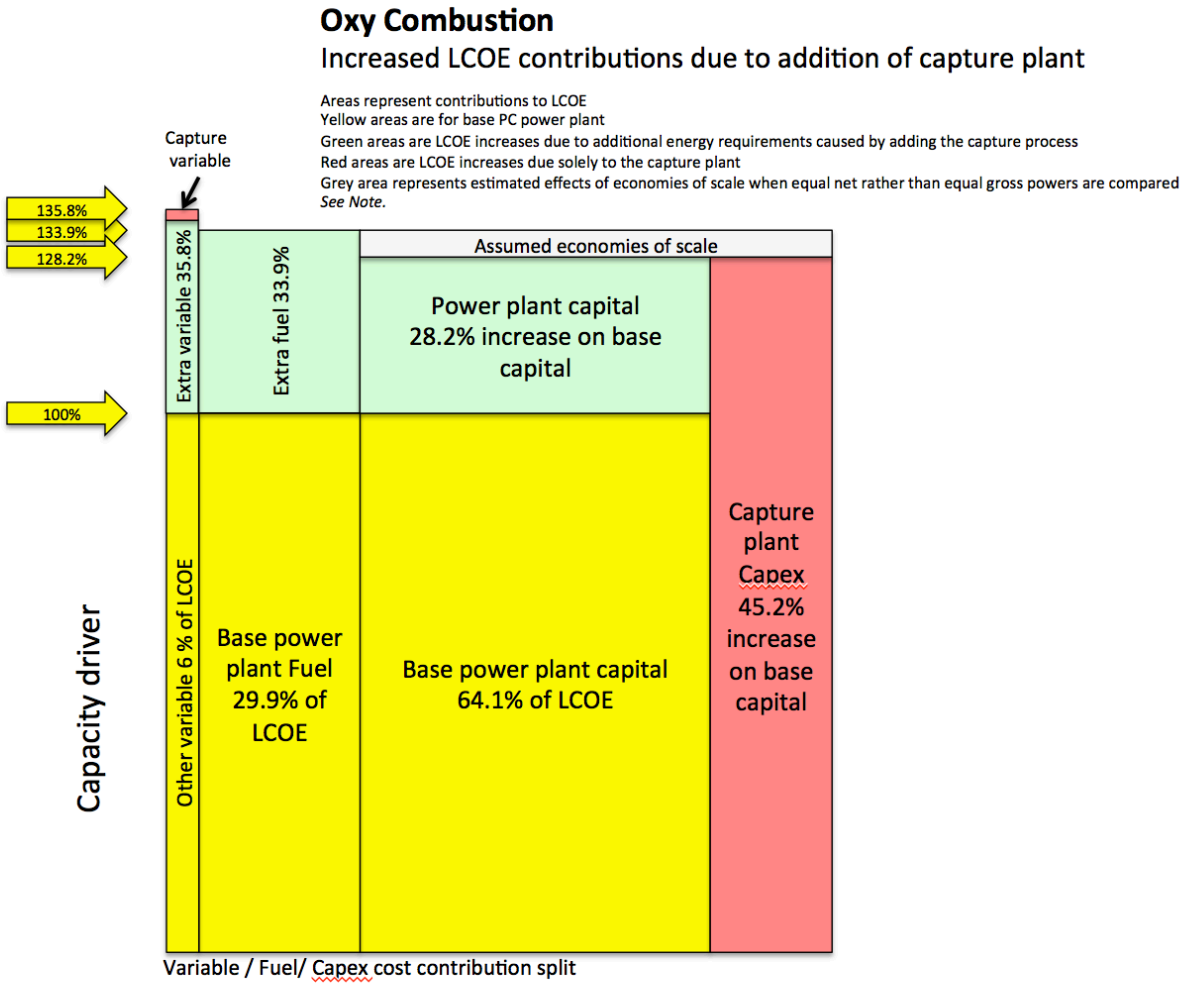


Figure 5 Oxy-combustion – contributions to LCOE increase

Solid looping systems

Solid looping technologies are at a much earlier stage of development in that there is no detailed evaluation of a baseline system utilising these technologies. It is only recently that data collected from larger MW scale pilot plants has been collected and could be used for making such estimates. As the processes will use large fluidised or fixed bed reactor systems making accurate cost estimates of these components will be difficult. The technology readiness level assessments given in Table 5. The scope for LCOE reductions cannot be assessed accurately at present, only general indications of potential are thus given in the table.

In making TRL assessments, the ability of the various test and demonstration systems to meet sufficient levels of complete volatiles combustion in the fuel reactor and solid sorbent/oxidant performance have been taken into account.

Table 5 TRLs and LCOE reduction prospects – Solid looping

Technology	Capture process type	TRL	Prospects to reduce the LCOE increase for capture
Calcium carbonate looping (CaL)	Post plus oxy	6	Potentially significant but more detailed evaluations needed
Indirectly heated calciner CaL	Post	3	Potential may be greater than for basic CaL process
H_2 production using CaL	Pre	1	Early claims of 9-12% reduction
Sorption enhanced reforming (SER)	Pre	1	Too early to assess
ENDEX (as pressure change CaL)	Post	More work needed	Too early to assess
CaL in cement production	Post	Same as for CaL	Too early to assess
Chemical looping combustion (CLC)	Indirect oxy	2 (low due to issues to be resolved)	Potentially very large reduction (coal only)
Chemical looping gasification (CLG)	Indirect oxy	1	Potentially very large reduction
Chemical looping with oxygen uncoupling (CLOU)	Indirect oxy	1	Potentially very large reduction (coal only)
Syngas CLC	Indirect oxy	1	High capital appears to counterbalance large efficiency gains
Coal direct chemical looping (CDLC)	Indirect oxy	1	Potential to roughly halve LCOE increase
Steam reforming CLC	Indirect oxy	1	N/A as this is a H_2 production process
Autothermal reforming (a-CLR)	Indirect oxy	3	N/A as this is a H_2 production process
Limestone chemical looping (LCL)	Indirect oxy	4	Developer claims up to 80% reduction (needs detailed validation)

The main observation is that calcium looping is much more advanced than chemical looping combustion even though both processes use very similar equipment. Indeed, the pilot plants are often able to operate using either process. A key point is that CLC could offer exceptionally good performance for coal-fired applications but not for gas-fired, since it cannot be configured to reach the high temperatures needed for efficient gas turbine operation. To date, operating with sufficiently complete combustion of coal has been elusive. Thus even though most of the equipment needed is at a higher stage of development, a viable design for the fuel reactor which will enable full combustion has to be found. Limestone chemical looping which is a similar process to mainstream CLC but uses a different type of oxygen carrier is noticeably more advanced and currently has an aggressive development programme.

Overall conclusions

A wide range of alternative CO_2 capture technologies has been reported. There may be significant differences between claims of the developers and the practicality, which this study has attempted to highlight. Amongst the many R&D initiatives there are several which stand out usually because of their favourable thermodynamics allowing reduction of the energy efficiency penalty. Of particular note are proposals which have been made for system configurations where recycles are created to concentrate CO_2. This allows simpler, lower cost separation processes which do not work well on low concentrations of CO_2 to be included in overall schemes.

Figure 6 below shows, in light green, the potential for LCOE reduction of some of the more promising technologies for post-, pre- and oxy-combustion capture which have emerged from the analysis. The reductions shown must be interpreted as rough assessments of the potential. Note that the baseline oxy-combustion process starts with approximately 20% advantage over the baseline post- and pre-combustion processes in this analysis, indicated in hashed dark green, based on the particular references used in this study.

There are also very promising technologies in which CO_2 capture is a more integral part of the power generation process, such as solids looping combustion, alternative thermodynamic cycles and certain types of fuel cells. Solid looping technologies, and chemical looping combustion applied to coal has great potential to reduce both the parasitic energy consumption and the LCOE increase for CO_2 capture. However, these technologies are at too early a stage to quote numbers for potential reductions and also have to overcome some significant technological hurdles. Only technologies for which percentage reductions have been estimated are shown in Figure 6.

Direct reduction of the capital cost of the equipment used in the processes does not appear to be a significant target for innovation. This may be because the individual pieces of equipment used in most capture processes are mature products with little potential for further cost reduction. However, the capital cost of capture equipment is a major contributor to LCOE and research directed at reducing this cost may still yield some incremental benefits.

The more developed technologies appear, as perhaps expected, to be taken up and championed by large industrial concerns, which is understandable on the basis of their potential and also the high costs of demonstration and commercialisation. Committed and experienced industrial support on this scale is probably a prerequisite for moving any of the technologies beyond TRL-6.

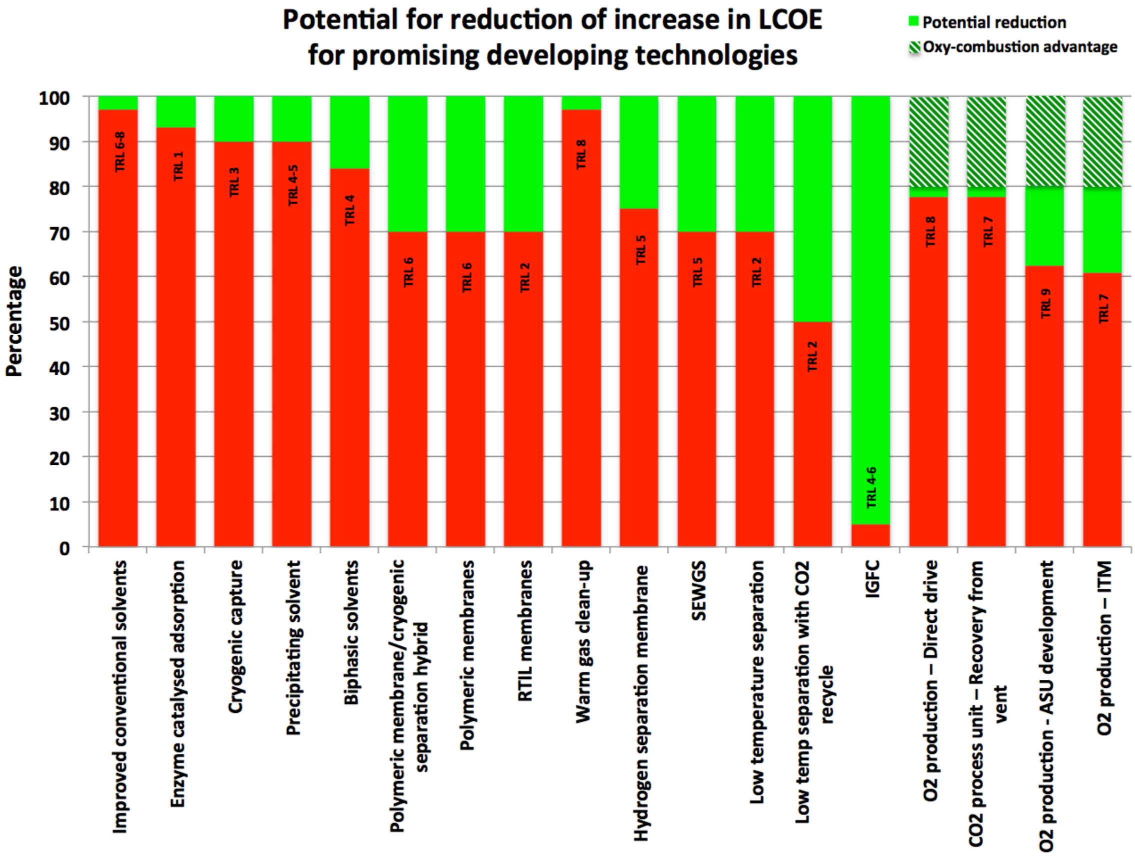


Figure 6 Potential to reduce the LCOE increase for CO_2 capture

Assessment of Emerging CO_2 Capture Technologies and their Potential for Cost Reduction

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1. Introduction

1.1. The need to reduce greenhouse gas emissions

The earth's atmosphere contains gases that are collectively called the greenhouse gases. The greenhouse gases are so called because in the atmosphere they both absorb and emit radiation. This process is the fundamental cause of what is termed the greenhouse effect [IPCC, 1990]. The main greenhouse gases in the earth's atmosphere are water vapour, carbon dioxide (CO_2), methane, nitrous oxide, and ozone. It is a well-established scientific fact that these greenhouse gases affect significantly the earth's temperature, without them, scientists predict that the earth's surface would average about 33 C° colder than the present average of 14 °C [Le Treut, 2007].

Since the late 18th century the atmospheric concentrations of these greenhouse gases and in particular CO_2 has risen by some 40%. The principal reason for the increase in global greenhouse gas emissions is the increased use of fossil fuels and global deforestation since the period we call the Industrial Revolution, the beginning of which is taken as the year 1750 [Le Treut, 2007]. The atmospheric concentration of CO_2 in the atmosphere has increased from 280 to 392.6 parts per million (ppm) in 2012. In May 2013 the atmospheric concentration of CO_2 at the Mauna Loa atmospheric observatory in Hawaii, taken as the "gold standard" atmospheric monitoring laboratory in the world, was recorded as 400 ppm. This is the first time that the atmospheric CO_2 concentration has reached 400 ppm in millions of years. Scientific analyses suggest that atmospheric CO_2 levels reached as much as 415 ppm during the Pliocene era, between 5 and 3 million years ago. In that period, global average temperatures have been estimated to be 3-4°C higher than the present average and as much as 10°C warmer at the poles. Sea levels have been estimated to have ranged between 5 and 40 m higher than today [SIO, 2014].

The principal effects of increased greenhouse gas concentrations in the atmosphere are:

- An uptake of energy by the climate system causing average surface temperatures to rise.
- Melting of polar ice sheets.
- Increased sea levels:

The other significant effect of increased atmospheric concentrations of CO_2 is ocean acidification. The ocean absorbs about a quarter of the CO_2 that is released into the atmosphere every year, so as atmospheric CO_2 levels increase, so do the concentrations of CO_2 in the ocean. Initially, scientists considered that there were benefits from the ocean removing CO_2 from the atmosphere. However, decades of ocean observations now show that there is also a downside in that the CO_2 absorbed by the ocean is changing the chemistry of the seawater, as more CO_2 is absorbed the pH of the ocean is increasing [IGBP, 2013].

The International Energy Agency (IEA) assesses on a regular basis the role that low carbon technological options can play in transforming the current energy system. The 2012 edition of the IEA's Energy Technology Perspectives [IEA, 2012] 2°C Scenario (2DS) identifies the technology options and policy pathways that ensure an 80% chance of limiting long-term global temperature increase to 2°C [IEA, 2012]. This IEA analysis shows that CCS is an integral part of any lowest-cost mitigation scenario where long-term global average temperature increases are limited to significantly less than 4°C, particularly for the 2°C Scenario (2DS). Figure 1 below provides a summary of the IEA's analyses of the impacts that each low carbon technology must achieve to attain the 2DS scenario.

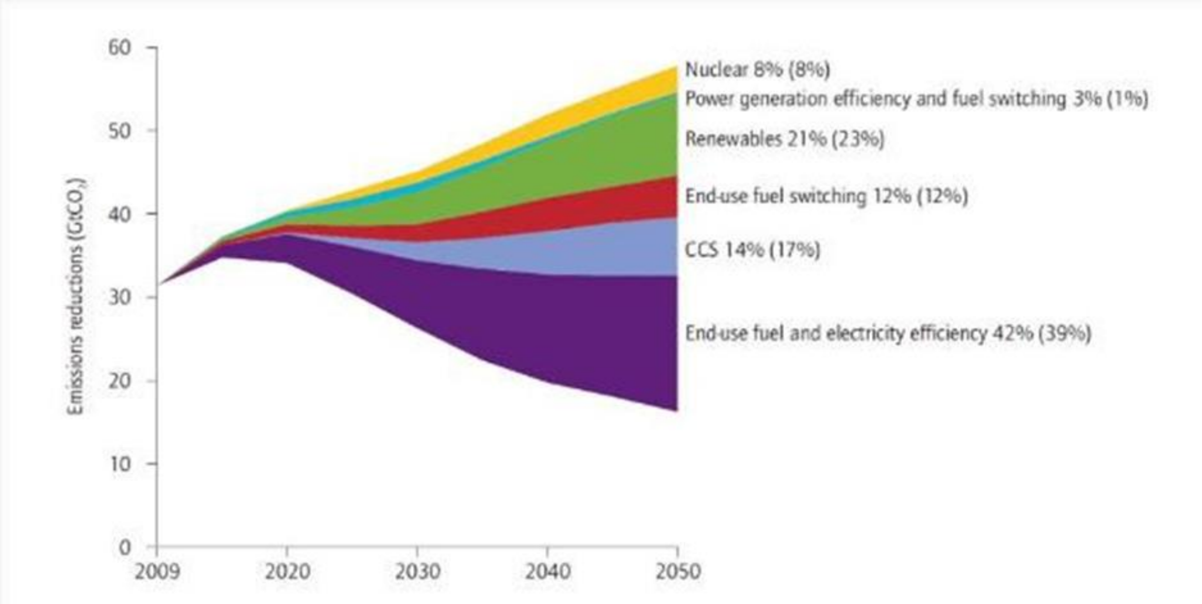


Figure 1 Contributions to emissions reduction (IEA 2DS Scenario)

The IEA's analysis indicates that a combination of low carbon technology options will need to be deployed globally to meet the 2DS target. There is no individual technology that can achieve the desired levels of emission reductions on its own. All the options on the table have their own merits and demerits. For carbon capture and storage (CCS), its advocates point to its ability to decarbonise the power sector without significant modification and investment in the current energy infrastructure. Detractors point to the energy efficiency penalty associated with the capture component and the storage integrity of geological reservoirs. More recently it has become accepted that CCS is probably the only technology on the horizon today that would allow industrial sectors (such as iron and steel, cement and natural gas processing) to meet deep emissions reduction goals.

The IEA indicates that abandoning CCS as a mitigation option would significantly increase the cost of achieving the 2DS. The additional investment needs in electricity that are required to meet the 2DS would increase by a further 40% if CCS is not available, with a total extra cost of USD 2 trillion over 40 years. Without CCS, the pressure on other emissions reduction options would also be higher.

More recently the IEA has considered a new scenario of 4DS. The 4°C Scenario (4DS) takes into account recent pledges made by countries to limit emissions and step up efforts to improve energy efficiency. Like the 2DS, the 4DS is already an ambitious scenario that requires significant changes in policy and technologies. Moreover, capping the temperature increase at 4°C requires significant additional cuts in emissions in the period after 2050. The need for CCS is not reduced in this scenario, rather its deployment needs to be ramped up quickly after 2020.

The IEA's analysis is not unique, one other example of many is the recent Global Energy Assessment [GEA, 2012] which uses a different assessment approach to that of the IEA which works from setting a “business as usual” base case also. The GEA study reports that there are many combinations of energy resources, end-use, and supply technologies that can simultaneously address the multiple sustainability challenges. One of the report’s key findings is that energy systems can be transformed to support a sustainable future through (a) radical improvements in energy efficiency, especially in end use, and (b) greater shares of renewable energies and advanced energy systems with carbon capture and storage (CCS) for both fossil fuels and biomass [GEA, 2012].

The combination of biomass and CCS (bioCCS or BECCS) is one that is being taken up by environmental groups because of its potential to take emissions out of the atmosphere and reduce the atmospheric carbon budget, the so called “negative emissions” effect. Recent work to assess the global potential for bioCCS has suggested the global technical potential is large and, if deployed, could result in negative emissions of up to 10 Gt of CO_2 equivalent annually. The key obstacle to the implementation of the technology is identified as the absence of a price for stored biomass based CO_2. There is therefore a need for policy developments in this area to assist global take-up of the technology [IEAGHG, 2011].

1.2. Background to the report

CO_2 capture is already well established in large commercial plants in various industries, particularly natural gas processing and chemicals and synthetic fuels production. In most cases the capture of CO_2 is an inevitable part of the industrial process and it is either vented to the atmosphere or it is used as a product, e.g. for enhanced oil recovery (EOR) or for food and drinks production. CO_2 capture is also starting to be demonstrated in large commercial power plants, for example a plant at Boundary Dam in Canada (post-combustion capture) started up in 2014 and another at Kemper County in the USA (pre-combustion capture) is due to start up in 2016. There are also plans to build commercial demonstration plants in the UK and DECC is funding FEED studies for power plants at Peterhead, Scotland (natural gas combined cycle plant with post-combustion capture) and White Rose, Yorkshire (coal-fired oxy-combustion). Construction and operation of these plants is essential to demonstrate the viability of the full chain of CCS, to improve investor and public confidence in the technology, to start to develop a commercial business and to start the process of ‘learning-by-doing’. These plants will use first generation capture technologies but other technologies, which offer the possibility of improved efficiency and lower costs, are currently at an earlier stage of development and could possibly be used in CCS plants in the longer term.

One objective of this report is to assess what stage of development emerging CO_2 capture technologies have reached. Technology readiness level (TRL) is a measure of the development status of a technology which was developed in the 1990s by NASA. Other entities using the TRL system have provided additional descriptive language on top of the primary framework in order to better connect the level definitions to fit their particular industry or technology. EPRI has produced definitions of TRL levels for CO_2 capture, shown in Table 1 [Freeman, 2011].

Table 1 Technology Readiness Level (TRL)

Demonstration	9	Normal commercial service
	8	Commercial demonstration, full scale deployment in final form
	7	Sub-scale demonstration, fully functional prototype
Development	6	Fully integrated pilot tested in a relevant environment
	5	Sub-system validation in a relevant environment
	4	System validation in a laboratory environment
Research	3	Proof-of-concept tests, component level
	2	Formulation of the application
	1	Basic principles, observed, initial concept

These definitions of TRL are used throughout the report. TRL level is not necessarily an indication of the timescales until commercialisation because it does not indicate the difficulty of overcoming the remaining development issues.

The report includes an overview of cost reduction for CO_2 capture technologies in general, which draws on discussions at CCS cost workshops organised by IEAGHG and others. Examples of technologies under development for post-combustion, pre-combustion, oxy-combustion, and solid looping processes for capture of CO_2 at power plants are reviewed, and new technologies specific to non-power industries are also discussed. The reviews quantify, where possible, the potential cost improvements, although it is emphasised that estimation of costs for new technologies is subject to considerable uncertainty.

2. Cost Progression for new technologies

Costs of CO_2 capture, in common with many new technologies, are expected to reduce in future due to a combination of ‘learning by doing’ and development, but estimating future costs of new technologies is subject to considerable uncertainty. Techniques that are used to estimate cost reductions include ‘learning curves’, engineering assessments and parametric modelling.

2.1. Cost learning curves

Continuing cost reductions, mainly due to ‘learning by doing’ and incremental improvements, are well recognised for a wide range of different technologies. It has been observed that the rate of cost reduction remains approximately constant for each doubling of installed capacity, although this is just a correlation and does not explain the reasons for cost reduction. The rates of cost reduction have been significantly different for different technologies. Indeed it should also be noted that costs do not always fall over time when the extent of deployment of a technology increases. A particular example is nuclear power, where costs have increased in real terms over the last 40 years, i.e. ‘negative cost learning’, despite a large increase in deployment and continuing predictions that costs would fall [UKERC, 2013]. It is therefore difficult to predict the rate of cost reduction that could be achieved by CO_2 capture processes. Historical information is available for technologies that could be considered to be analogous to some extent to CO_2 capture technologies, such as Flue Gas Desulphurisation (FGD), Selective Catalytic Reduction (SCR), oxygen production and liquefied natural gas (LNG) production but there is still no guarantee that the learning rates for these processes would apply to CO_2 capture processes [IEAGHG, 2006].

An important factor when predicting cost reduction is the extent of current deployment, which is used as the baseline when calculating the doubling of installed capacity. Many of the components used in CO_2 capture processes are already widely used in other types of plants, for example air separation plants, gas compressors and coal fired boilers. For the purposes of calculating learning cost reductions a capture plant could be regarded as a single unit with an overall learning rate or a collection of sub-units each with its own learning rate, depending on the installed capacity of that type of unit in other applications as well as in capture plants. The extent to which components used in CCS processes can be considered to be ‘new’ is an uncertainty if they are modifications of designs that are currently used. For example, oxy-combustion boilers are a modification of conventional air blown boilers and CO_2 compressors are a variant of other large gas compressors. The overall system may be regarded as ‘new’ and hence subject to learning cost reduction, even if the components are already widely used in other applications.

Evidence of technology cost reductions are often masked or accentuated in the short term by external factors. The supply/demand balance for materials, equipment, specialist labour and services can affect production costs. The availability of subsidies etc. can also affect the price charged for the finished equipment or plant. Costs may appear to increase in the short term due to these market factors even though there is a continuing long term trend of cost reduction, and conversely the market factors may accentuate the cost reductions in the short term. Fluctuations in exchange rates and corrections used to account for general inflation, to convert costs to a constant money value basis, can also affect perceived costs. Another significant external factor can be increasing regulatory requirements, which can result in increased costs.

Although costs of new technologies tend to reduce when they are used at a greater scale, the projected costs tend to increase during the time that a process is being developed, reaching a peak around the time when the first large scale plants are built or shortly afterwards, as shown in Figure 2. This can be explained for example by general optimism by the researchers, a need to demonstrate large benefits to obtain development funding, inadequate knowledge of the scope of equipment required, the absence of adequate engineering designs for large scale units and the inability to achieve performance targets. Figure 2 shows costs reducing immediately after the first plant but sometimes costs remain high for early plants and there is a delay before the cost reduction for each doubling of installed capacity commences [IEAGHG, 2006]. Note this figure is purely illustrative and it is not intended to be an accurate indication of the magnitude of cost variations.

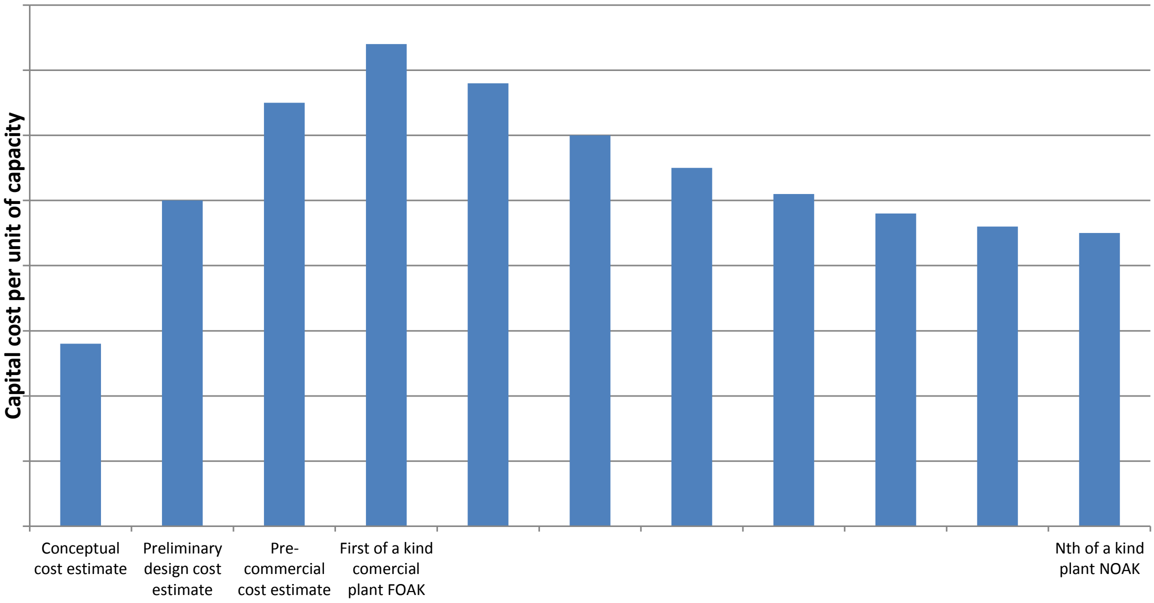


Figure 2 Capital cost learning curve

It has been suggested that learning curves actually consist of two elements, ‘learning by doing’ and ‘learning by researching’ [UKERC, 2013]. In some cases the cost reductions that occur may be more a function of the amount of research that takes place during the time that the rate of deployment increases, rather than being directly the result of learning by doing due to increased deployment but it can be difficult to obtain the data on research expenditure to construct two component learning curves.

Costs of production, e.g. cost of electricity or cost of emissions avoidance, may reduce when CCS becomes successfully demonstrated because the perceived risks for investors become lower, financing becomes easier and the required rates of return become lower. There are also expected to be significant reductions in the costs of CO_2 transport and storage due to the development of integrated transport networks, although over the longer term a need to use more distant and less favourable storage reservoirs may result in cost increases. These types of cost reduction are not considered in this report but in a recent report by the UK CCS Cost Reduction Task Force [Cost Reduction Task Force, 2013] they are the two largest reasons for cost reduction of CCS plants in the time scale they considered, i.e. until 2028.

2.2. Engineering assessment of cost reduction for new technologies

Cost learning curves are usually based on learning by doing and incremental improvements. Development of a substantially different technology may result in an additional step change cost reduction, although in the short term it may also result in a backward step up the cost learning curve, so the full benefits of the new technology compared to the current technology may only be achieved in a longer timescale. This report focusses on the long term reductions in costs of new capture technologies compared to baseline current technologies.

There are various measures of the costs of CCS, as discussed in a report produced by a working group set up during a series of workshops on CCS costs, which have now evolved into IEAGHG’s CCS Cost Network [IEAGHG, 2013]. The most commonly used measures of the costs of CCS are capital cost, levelised cost of electricity (LCOE), the increase in LCOE due to the addition of capture, and CO_2 avoidance cost. Capital costs can be expressed as total plant cost, including contingency, or total capital requirement, which also includes interest during construction, owner's costs, working capital and start-up costs. Costs of CCS should normally include the cost of CO_2 transport and storage, as transport and storage is an essential part of CCS. However, when considering the costs of new capture technologies compared to current technologies it is simpler to exclude transport and storage costs and that is the basis used in this report.

Assessment of new capture technologies tends to focus initially on efficiency because this can be evaluated scientifically and because the consequence of extra energy consumption is large, and in some cases it contributes the largest part of the cost of capture. Discussions at IEAGHG's Cost Workshops have indicated that this may be the most meaningful metric for assessing early stage capture technologies because the lack of large scale process and equipment design information may make cost estimates meaningless. The first stage in the assessment should be to look at whether the process is potentially technically feasible, based on thermodynamics, kinetics, complexity etc. and only look at costs later. This approach is taken in this report when meaningful cost information is not available. Examination of detailed cost estimates for plants with capture shows that the greatest effect of reduced efficiency is not usually the extra cost of the fuel but the capital charge which accrues for the extra plant needed to consume the fuel, generate the electricity and process the additional flue gases which are created.

As discussed earlier, costs of new technologies often increase until the time when large commercial plants are built. Sometimes large 'process contingency' factors are used in cost estimates to allow for incomplete estimates of the amount of equipment required and optimism in system performance predictions but the use of high process contingencies may bias cost estimates upwards inappropriately for new processes, resulting in the early rejection of technologies that may in practice be able to achieve significant cost reductions. Another way in which this underestimation is compensated in some studies is to use higher risk factors when calculating the capital charge during LCOE estimation.

Costs of new technologies are usually compared to a baseline technology, for example to show a percentage reduction in the cost of electricity, the incremental cost of electricity due to capture, or the cost of CO_2 emissions avoided. Selection of the baseline is an important issue. The baseline should be the best currently available technology but it should be noted that the costs of the baseline will improve over time due to general cost learning effects, incorporation of incremental improvements and greater optimisation. Developers of new technologies sometimes select an unfavourable baseline or a baseline based on old technology to show a high cost reduction for their new technology. Ideally a common baseline would be used for assessment of all new technologies but that is not always possible. In many cases cost improvement data for new technologies from published references has to be used and the details of the baseline case are not always clear. In this report a somewhat conservative approach has been taken when considering baselines for steam conditions and class of gas turbine. However, the adoption of more advanced conditions usually has positive knock-on effects on the costs of capture.

2.3. Methodology for comparison of capture costs.

In the face of the above mentioned difficulties in assessing and comparing costs a methodology has been developed for the purposes of this report in order to be able to make meaningful comparisons of the various capture technologies which are under development.

Comparing capture costs is complicated as there are different ways of performing capture with differing operating and capital cost structures. The costs of the three main conventional technologies have been estimated and compared and these form a useful benchmark for calibrating the costs of new capture technologies. This is for two reasons, firstly their costs can be broken down into a number of elements and some of these are common to other processes, especially those which are hybrids of the main ones. Secondly there are only a limited number of ways in which the CO_2 end product of combustion with oxygen derived from air can be isolated. Different approaches to the key separations can thus be compared and relative costs estimated.

As noted earlier, costs can be reported in several ways for comparison. The most useful are costs per tonne of CO_2 and this can either be the gross amount captured or the amount avoided. The latter is a better measure of the effectiveness of a process for emission reduction. The other main metric is the levelised cost of electricity, which is useful when comparing capture processes in the power industry and is one which gives a much better feel as to the costs relative to business as usual. It is calculated using discounted cash flow at a constant present day electricity cost which gives zero net present value with a constant discount rate and no tax. Thus the LCOE will be adopted as the main metric in the rest of this report. There is a clear distinction between COE and LCOE. The latter is based on discounted cash flow (DCF) calculations with no allowances for inflation over time. When examining cost methodologies it is thus important to identify whether any allowances for inflation of cash streams such as fuel or labour have been made or whether the declared discount rate has been adjusted for effects of inflation. For a true comparison between technologies all of the key factors used in the DCF calculation such as discount rate plant operating lifetime etc. should be identical. (Table 2 illustrates that different organisations do use slightly different discount and inflation assumptions) A feature of all the estimates is that the costs are made up of capital and operating costs and usually these two elements are of similar size. Longer term, when the capital investment in a plant has been written off, the operating element will be of greater interest. It is this on-going operating cost which will determine whether it is viable to keep the capture plant in operation. Part of this on-going cost though is related to the original capital cost as this is usually in proportion to many elements of the on-going maintenance costs.

During combustion, essentially a fuel containing both hydrogen and carbon is oxidised with oxygen from the air which is of course mixed with nitrogen. The end products are water and CO_2 mixed with any residual components of air which are left after the combustion process which has been used. Without the nitrogen and other inert gases in the air the recovery of CO_2 would be easy as the water formed can simply be condensed. The problem of CO_2 capture is thus more about nitrogen separation.

In post-combustion capture nitrogen, some residual oxygen and water in the form of steam are separated from CO_2.

In oxy-combustion most of the nitrogen is separated from air before combustion leaving only water/steam and some residual nitrogen, argon and oxygen to be separated from the CO_2.

In pre-combustion capture some nitrogen is separated from air but the main separation of CO_2 is from hydrogen and steam.

In all processes the separation from steam or water product occurs mainly through cooling and condensation but all need to have a further drying step to produce sufficiently dry CO_2 to avoid corrosion during transport. Those processes which use cryogenics for CO_2 processing will generally need deeper drying to avoid equipment blockages due to ice formation.

Novel processes and hybrid processes can thus be analysed to determine what separations are used and to do this it is useful to look not just at how CO_2 is separated but also how the other substances, i.e. N_2, O_2, H_2, H_2O are separated. In this way it is possible to identify how the alternative approaches to these separations, when compared to those used in the conventional capture processes, will compare in terms of both cost and thermodynamic efficiency. This allows a judgement to be made as to the potential for overall cost reduction as compared to the benchmark processes.

This approach will assist with calibrating estimates against one another. This differential costing approach has been successfully applied for example in analysing the value of additional heat integration of the CO_2 compression system with the main capture processes in a study for IEAGHG carried out by Foster Wheeler [IEAGHG 2011a].

Combustion of fossil fuels also results in production of impurities and inerts, most notably sulphur compounds and nitrogen compounds. Ash and mercury are the other most significant contaminants. These compounds also have to be handled in the processing to avoid emissions to atmosphere and in some cases to protect the CO_2 removal processes. The separations used for these compounds can be included in the analysis.

In addition to separations of components various reactions are carried out on the fuel. In simple power generation processes there is a single complete combustion reaction. However, other processes employ a sequence of reactions and these may involve additional substances. Integrated gasification combined cycle (IGCC) splits the combustion into two stages, gasification followed by syngas combustion. In pre-combustion capture an additional shift reaction is added. Solid looping technologies introduce metal oxides and carbonates as intermediates, for example chemical looping combustion (CLC) involves two reactions: oxidation of a solid oxygen carrier and reaction of this with the fuel. Mapping both the reactions and separations assists in classifying the technologies for cost comparison purposes.

The comparison will thus proceed using the following initial steps.

- Classify processes by the separations and reactions used
- Select a benchmark process for each of the main capture routes
- Identify which benchmarks are applicable for each of the novel or developing processes

The next step is to analyse a detailed cost estimate for each of the benchmark processes to identify the main elements which increase cost of electricity. Interdependencies and their relationship to efficiency will also be assessed. It will also be necessary to identify any key assumptions which are made, so that costs can be normalised if these differ between estimates. The importance of these steps is illustrated by consideration of a detailed cost estimating study made by the US NETL [NETL 2012], which compares costs of power generation from coal without capture, with conventional post-combustion capture and with two developing technologies – CO_2 membranes and pressure swing adsorption (PSA).

Examination of cost estimates for pulverised coal (PC) power plants, with and without conventional post-combustion capture, reveals the effect which the addition of capture has on the various components of the estimate. It is important to understand how these effects are distributed in order to appreciate how new technologies might reduce costs. In the case considered, plants with equal net power output were compared requiring that many of the components for the capture plant have larger capacity. The estimate reveals that about 66% of the capital cost increase is due to the additional compression and capture equipment whilst 33% is due to increases in the coal handling, boiler, generator and utility systems needed to compensate for the auxiliary power and heat loads. Furthermore, these indirect increases are not distributed equally but depend on the extent to which the added capture process imposes additional capacity on these various components. In the example the coal feed is increased by a factor of 1.38 because more fuel is needed to generate additional power and to provide stripping steam. On the other hand, the gross power output of the turbine/generator set increases only by a factor of 1.14, reflecting the smaller percentage increase in electrical auxiliary power as compared to use of thermal energy for the solvent regeneration.

These capacity increases do not necessarily translate into proportional cost increases. In the case of the NETL 2012 estimate the coal handling facilities increase in cost by a factor of only 1.23, whereas the handling capacity is up by a factor 1.38, implying a scale up exponent for cost of about 0.63. The water system is increased in raw capacity by a factor of 1.9 while costs are only 1.63 higher, implying a scaling exponent of about 0.76. The choice of scaling methods for the necessary increase in capacity does thus have an effect on estimates of the additional cost of adding capture. Choosing lower scaling exponents, either as the estimating method or as a result of actual quotations, would result in reduction of the additional costs.

In the case of adding capture to a gas turbine based power plant the option to incrementally increase the size of this portion of the equipment is not available since the turbines are of fixed power rating. In that case the comparison has to be made on the basis of equal gross gas turbine powers, which will result in larger differences between the LCOE in capture and non-capture cases. The magnitude of the effect of the scale factor assumption can be calculated by adjusting the cost figures for the main elements to be linear with the appropriate capacity change with values chosen from fuel input, generator power or water consumption where appropriate. This results in a further 25% increase relative to baseline no capture costs so is not insignificant. The capital increase before owners and financing costs for adding Fluor's Econamine FG Plus process to a 550MW PC station was estimated (NETL 2012) at about 75% but would be about 100% if account is not taken of economies of scale.

The above insights into the capital cost structure need to be taken into account when making comparisons of capture technologies. For the purposes of this report the costs will be adjusted to reflect those for plants of equal gross thermal capacity, i.e. of equal fuel consumption. To do this a set of cost/capacity scaling exponents will be chosen for the different elements of the plant for use when such scale effects need to be taken into account.

A further issue that arises is the way in which capital expenditure (CAPEX) is reflected in the cost of electricity. The "capital charge" which is calculated will depend on several factors, notably, stream factor, project lifetime and financing structure. The financing structure affects the "cost of capital" because estimates sometimes assign higher costs of borrowing for more risky technologies. For this study the basis for cost comparison should be nth of a kind (NOAK), which means that the cost of financing will be adjusted to be equal to that for conventional power plant.

2.4. Cost comparisons – breakdown into elements

The extra cost of producing electricity for a plant fitted with capture is generally divided into two main components. Those for additional equipment and those for capacity increases in the base plant due to increases in use of auxiliary power and/or thermal energy. In some cases major sections of a conventional plant may be replaced by alternative power generating technology (for example a fuel cell) and usually there will be larger overall capacity to provide the extra auxiliary energy streams needed to drive the separation processes. The cost comparison will thus identify the main sources of difference in these two categories, i.e. extra separation processes and additional energy production.

The cost of electricity is made up of the capital element and the variable element. The variable element is made up of three main components; fuel, other variable operating expenses such as chemicals and consumables, which are dependent on production, and a fixed element which includes such things as operating and maintenance labour. A proportion of any increase in the fixed costs could be attributed to higher overall capital cost and a proportion of the variable costs could be attributed to the higher requirement for auxiliary energy. For the existing well established post-, oxy- and pre-combustion alternatives the cost increases for capture will be broken down and attributed to these categories. For the emerging technologies the effect on costs will be assessed in the same way, as far as the currently available information allows. In the next section the breakdown of costs for the conventional capture benchmark technologies is described.

2.5. Cost comparisons – relationship between LCOE increase and cost of CO_2/tonne

The LCOE increase is used as a key indicator for comparison. However, sometimes there is interest in the actual cost per tonne captured and particularly per tonne avoided as this can be related to prospects for CO_2 emission certificate prices. Rather than quote both figures the relationship between these two values is presented here, as this can be related to the LCOE increase and the baseline emissions and the ratio between baseline and capture plant electrical efficiency.

The cost per tonne avoided is the cost increase per kWh divided by the CO_2 avoided per kWh. This latter is the baseline emission per kWh less the baseline emission times the ratio of efficiencies baseline/capture plant times the uncaptured fraction.

E_b = baseline emission g/kWh

Eff_{base} = baseline efficiency

Eff_{cap} = capture plant efficiency

C = captured fraction

Cost per tonne avoided = (LCOE increase \$/MWh) / ($E_b - E_b \times Eff_{base} / Eff_{cap} \times (1-C)$) $\times 10^3$

For post-combustion the baseline example has E_b = 802 g/kWh, Eff_{base} = 39.3% , Eff_{cap} = 28.4%, C = 0.9. LCOE increase is 44.4 \$/MWh, so that cost of CO_2 avoided is \$64.3/tonne.

2.6. Using LCOE increase to estimate cost of CO_2 avoided

Because of the close relationship between LCOE and cost of CO_2 avoided it is possible to estimate the latter with reasonable accuracy if the percentage LCOE increase is known and also the cost and efficiency of an appropriate baseline plant. Figure 3 below is an example and allows this conversion to be made for capture processes which are adaptations from a baseline of a coal-fired PC plant.

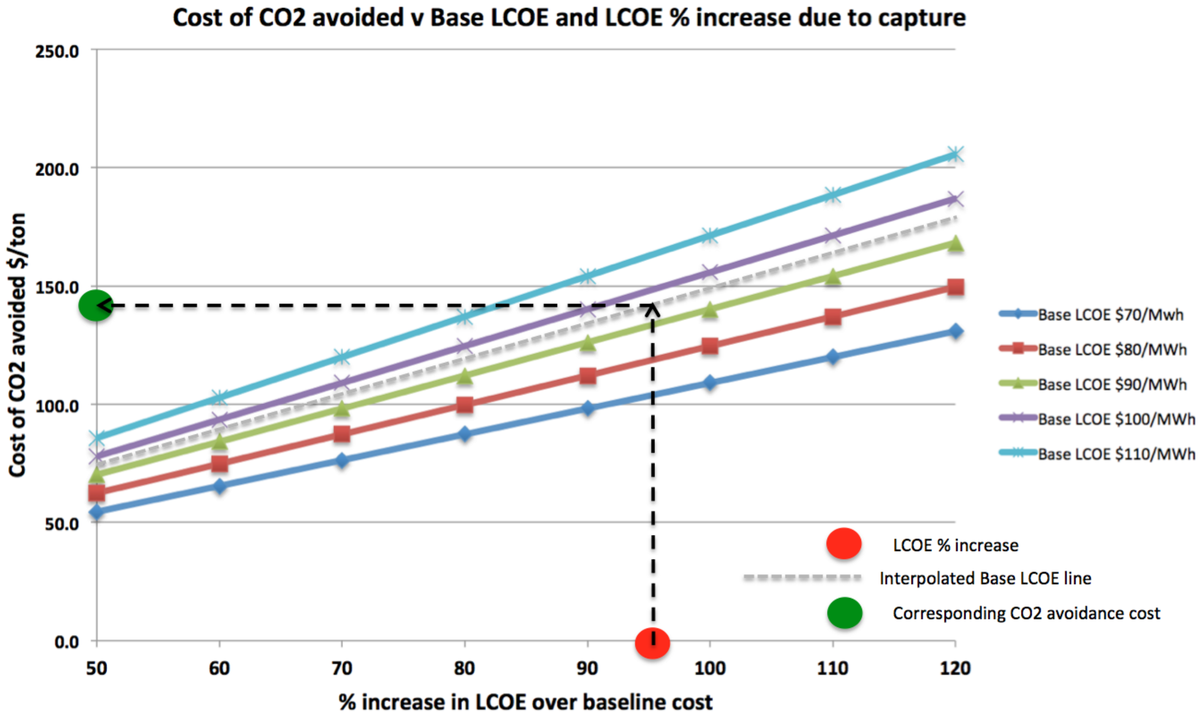
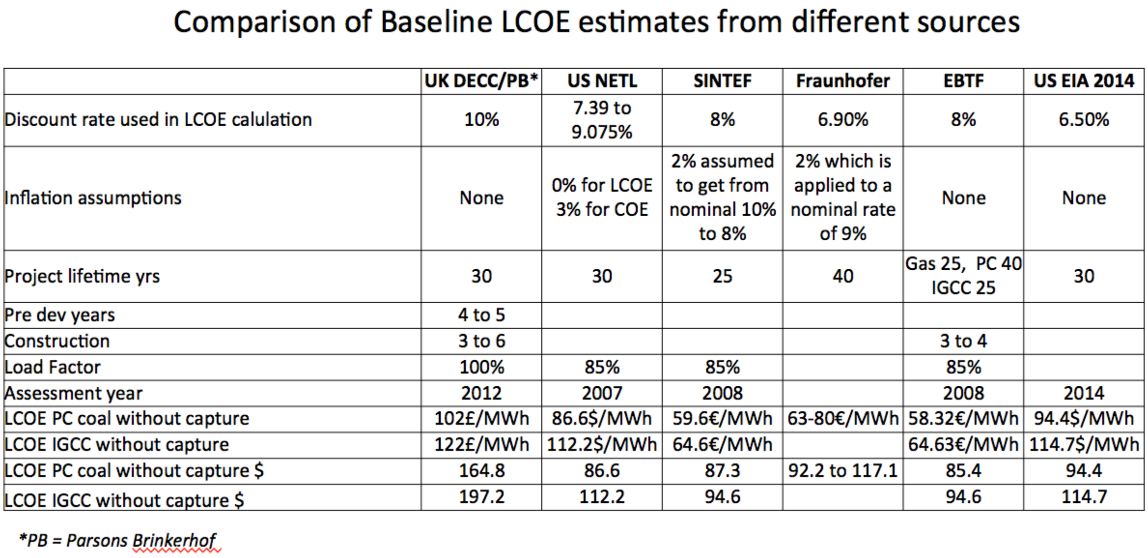


Figure 3 Cost of CO_2 avoided v base plant LCOE and LCOE% increase due to capture

Although the cost of CO_2 capture can be derived from the increase in levelised cost of electricity (LCOE), the plant electrical efficiency and the carbon content of the fuel; unlike the metric of percentage increase in LCOE; it is an absolute measure which will vary according to currency, region and year of the estimate. Furthermore, the assumptions on which the LCOE calculations are based will also introduce variations. The variations which might be found in the latter are illustrated in Table 2, which summarises some of the key assumptions used by DECC, SINTEF, NETL, US EIA, EBTF and Fraunhofer Institute in recent studies [DECC 2012, Jordal 2012, NETL 2012, US EIA 2014, CAESAR 2011, Kost 2013].

Table 2 Comparison of baseline LCOE estimates from different sources



Comparison of Baseline LCOE estimates from different sources

	UK DECC/PB*	US NETL	SINTEF	Fraunhofer	EBTF	US EIA 2014
Discount rate used in LCOE calulation	10%	7.39 to 9.075%	8%	6.90%	8%	6.50%
Inflation assumptions	None	0% for LCOE 3% for COE	2% assumed to get from nominal 10% to 8%	2% which is applied to a nominal rate of 9%	None	None
Project lifetime yrs	30	30	25	40	Gas 25, PC 40 IGCC 25	30
Pre dev years	4 to 5					
Construction	3 to 6				3 to 4	
Load Factor	100%	85%	85%		85%	
Assessment year	2012	2007	2008		2008	2014
LCOE PC coal without capture	102£/MWh	86.6$/MWh	59.6€/MWh	63-80€/MWh	58.32€/MWh	94.4$/MWh
LCOE IGCC without capture	122£/MWh	112.2$/MWh	64.6€/MWh		64.63€/MWh	114.7$/MWh
LCOE PC coal without capture $	164.8	86.6	87.3	92.2 to 117.1	85.4	94.4
LCOE IGCC without capture $	197.2	112.2	94.6		94.6	114.7

**PB = Parsons Brinkerhof*

Note the variation in assumptions for discount rate and plant operating lifetime and the variations in the LCOE which the different studies report as a result. It is thus recommended that capture costs are compared by first evaluating the % LCOE increases reported and then converting these to costs per tonne using the same baseline LCOE.

2.7. Improving cost comparisons between diverse CO_2 capture technologies

Although much literature is available on costs of emerging technologies it would be useful if future estimates could be guided towards use of a more consistent basis, making comparisons more meaningful. In order to do this a methodology for generating costs is proposed which makes use of cost elements which are common to the processes being compared.

The conventional approach to making cost estimates is to identify the size and characteristics of all the main pieces of process equipment for a plant fitted with capture and a reference plant without capture. This means that a process flow scheme has to be developed along with basic heat and material balances. This can be an expensive and time consuming task and estimating the cost of novel types of equipment can be difficult. The task can be somewhat simplified once the cost consequences of adding parasitic power have been analysed, as that element of cost increase can be estimated as a percentage of that for the baseline plant. This does however require a thermodynamic analysis of the process to identify exactly what the parasitic thermal and electrical load increases will be. However, this is potentially simpler than developing a full process design for the power plant.

A simple estimate of the rest of the capture plant could then be made on a parametric basis by breaking it down into a number of complete sub-systems for which individual costs might be found. Sub-systems which might be amenable to this approach are ASU's, low pressure (LP) and high pressure (HP) gas liquid contacting systems, refrigeration systems and CO_2 compression/drying. A good example is air separation where the cost of an ASU could be roughly estimated as a function of its oxygen capacity. This approach does not of course allow investigation of developments in ASU technology for which more detailed estimating methods would be needed. However, many capture processes, for example calcium looping, IGCC, and IGFC, utilize a certain amount of oxygen and optimization of the ASU is not the main driver of cost reduction. Similarly, gas/liquid contacting units' capital cost could be estimated simply as a function of the flow of treated gas. Refrigeration systems could similarly be treated as a process block for estimating purposes with refrigeration duty and lowest temperature as key variables. The coefficient of performance (COP) of refrigeration systems is closely linked to the cold temperature required, enabling simple estimates to be made of the power consumption for compression based systems.

Allowance can be made for easily identifiable secondary cost drivers such as oxygen purity with information often readily available from the literature.

The great advantage of this systems approach is that the alternative of a bottom up, item-by-item equipment approach often results in different results for the same basic system and is also much more time consuming to undertake.

The proposed approach for comparative assessment across a wide range of diverse processes is illustrated in Figure 4. The aim is to minimize repeats of detailed cost engineering on those parts of the system where it is not needed and where doing so may even reduce the comparability of overall estimates.

Where parts of the capture plant cannot be represented by standard systems, an equipment based cost estimating approach is all that is left. Here it is also possible to work at higher levels by grouping the remaining equipment into broad categories. A first split could be between rotating equipment and fixed equipment; and fixed equipment being subdivided into heat exchange and vessels, the latter covering all columns, reactors, fluidized beds, adsorbers etc. Power, area and volume can be the primary cost drivers and a cost factorial approach used to account for different subtypes, internals, fills and materials of construction. Scaling exponents should also be used the same way as for complete sub-systems. Since the percentage of the costs attributable to parts of the process estimated in this way may be quite small, estimates can be rough without unduly affecting overall cost comparisons.

There remain a few processes that are fundamentally so different from the conventional power generation process, that only stand-alone detailed engineering estimates can be used and a step-out approach is not possible. For example processes involving fuel cells, fluidised beds or novel turbines.

In summary, a simple cost comparison system is proposed based on two elements. The first is an estimate of the costs of the parasitic power and the second an estimate of the capital and direct consumables costs for the capture facility. For the second element, costs for complete subsystems should be sought wherever possible rather than using the more detailed equipment based method. An approach along these lines is described in a recent SINTEF report investigating hybrid cryogenic CO_2 separation systems [Jordal 2013]. A very simple system was developed some years ago by IEAGHG, specifically for the purpose of comparing novel capture technologies [IEAGHG 2005a]. It is however beyond the scope of this study to develop such a system any further.

The procedure described above is illustrated in Figure 4 below.

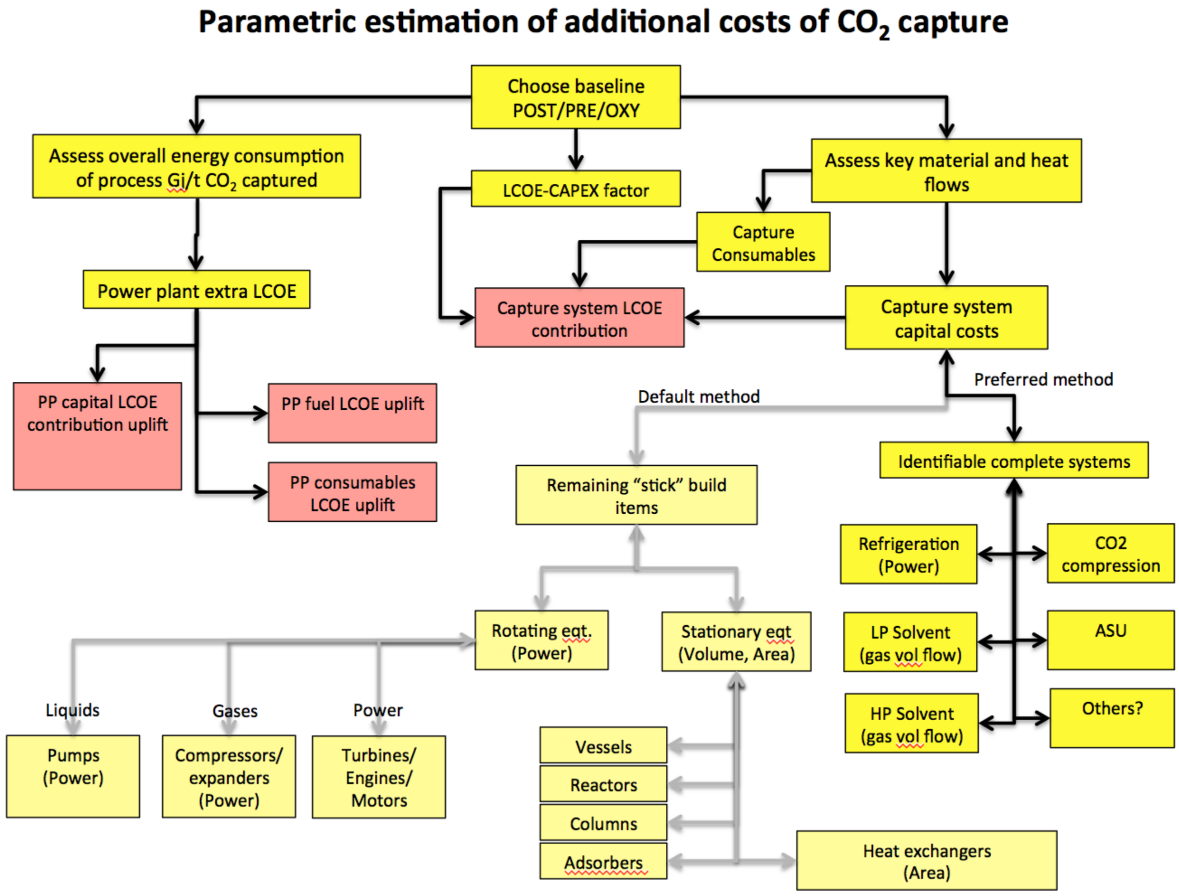


Figure 4 Parametric estimation of additional costs of CO_2 capture

2.8. Thermodynamic considerations

2.8.1. Combustion of fuel and conversion to work

When fuel is reacted with oxygen from the air in a process designed to convert the energy in the fuel to electrical power, only a portion of the free energy of the combustion reaction can be converted to power. Theoretically, in a reversible electrochemical process all of the free energy could be converted. This would be the ultimate potential efficiency for a fuel cell. However, the normal processes all rely on thermal energy to work conversion processes which have limits to their efficiency. The maximum efficiency for these processes is the Carnot efficiency, which is calculated as a simple relationship involving only the starting temperature at which heat enters the process and the temperature at which is rejected after extraction of work. The formula is $(T_{in}-T_{out})/T_{in}$. In practice, because of inefficiencies in turbo-machinery, processes are only able to reach about 73% of the Carnot efficiency.

The efficiency of processes is usually calculated on the basis of the amount of electrical energy produced divided by the heat of combustion, which is derived from the standard enthalpy of formation of the fuel. In fuels containing hydrogen the enthalpy change depends on whether the final product H_2O is in the liquid or gaseous phase. The former gives the higher heating value (HHV) and the latter the lower heating value (LHV). Note that the

Standard Gibbs free energy of formation differs slightly from the standard enthalpy of formation.

Thus the theoretical efficiencies for a perfect electrochemical conversion of pure methane, pure hydrogen and pure carbon fuels are as follows.

Table 3 Theoretical electrochemical conversion efficiencies of fuels

Combustion reaction	Free energy change ΔG_f^0 kcal/mol	Enthalpy change ΔH_f^0 kcal/mol	Theoretical efficiency
Methane to CO_2 and $2H_2O(g)$	191.3902	191.7588	99.81
Methane to CO_2 and $2H_2O(l)$	195.4998	212.7978	91.87
Carbon to CO_2	94.26	94.052	100.22*
Hydrogen to steam	54.6351	57.7979	94.53
Hydrogen to water	56.6899	68.3174	82.98

*> 100% as ΔG_f^0 is slightly greater than ΔH_f^0

Table 4 shows the theoretical efficiencies and practically attainable efficiencies based on LHV for combustion of pure methane, pure carbon and pure hydrogen. Attainable efficiencies are presumed to be 73% of theoretical Carnot efficiency which is typical of current technologies. The table also shows the typical temperature limitations which apply to gas turbines and steam boilers at present.

Table 4 Theoretical and practical efficiencies attainable from combustion based power processes (LHV basis).

	Adiabatic flame temp °C	Max. usable temp °C	Carnot efficiency %	Practical efficiency based on flame temp %	Carnot efficiency with temperature limitation %	Practical efficiency with temperature limitation %	Theoretical electro-chemical efficiency %	Theoretical electro-chemical to thermal advantage %
Methane air	1950	1500.0	86.1	62.89	82.63	60.3	91.87	5.7
Methane O_2	2810	1500.0	90.0	65.71	82.63	60.3	91.87	1.9
Anthracite air	2180	650.0	87.4	63.83	66.63	48.6	100.22	12.8
Anthracite O_2	2900	650.0	90.3	65.91	66.63	48.6	100.22	9.9
H_2 air	2210	1500.0	87.6	63.94	82.63	60.3	82.98	-4.6
H_2 O_2	3200	1500.0	91.1	66.53	82.63	60.3	82.98	-8.2

From the table it can be seen that there is a small efficiency gain of around 2.5% still available to air consuming gas turbines simply by raising inlet temperatures towards the flame temperature. Further gains would require other forms of improvement. Raising temperatures in steam boilers has much larger potential of nearly 18% but would require tube materials far beyond what is practical or affordable at present. Indeed current research (for example the European AD700 project) is aimed at a relatively modest increase to 700ºC. The last column shows the potential advantage of following an electrochemical route which is quite significant for methane. The same applies to carbon, although an electrochemical route involving solid fuel would be physically difficult to achieve even at laboratory scale. Interestingly the electrochemical route is less favourable for hydrogen, which certainly raises questions about the competitive efficiency of a fuel to hydrogen to electricity process route by a fuel cell.

2.8.2. Energy required for separation of gases

When two ideal gases are allowed to mix there is an increase in entropy and the free energy of the mixture is reduced. In order to re-separate them this free energy reduction has to be re-supplied to the gases in the form of work. The amount to be supplied is relatively modest but the processes which can be used to perform the separation are very inefficient so that many times the theoretical minimum has to be used. To illustrate this the theoretical energy required to separate oxygen is around 0.18 GJ/tonne depending on purity required whereas a cryogenic oxygen plant might consume 1 GJ/tonne. Thus 5 times as much energy has to be consumed as the work actually required for the separation. That does not mean that any practical process could approach this energy consumption. Firstly, the energy is in the form of work and even the best power plants are only 60% efficient which already sets an ultimate limit of 0.18/0.6 = 0.3GJ/tonne on the basis of fuel energy input. This energy then has to be utilised in processes such as compression where further losses are experienced. The main energy input to a cryogenic separation plant is as electrical power to the main air compressor. The overall efficiency of a large compressor may be only 80% because of frictional, electrical and aerodynamic losses so that the ultimate limit is already reduced again to 0.3/0.8 = 0.375 GJ/tonne. Thereafter there are losses because of temperature differences in heat exchange and in the distillation process.

Similarly, recovery of most of the CO_2 from the flue gases of a coal plant requires a free energy change of about 0.15 GJ/tonne, whereas typical processes will consume 2.5 to over 4 GJ/tonne. The two main reasons for these very low thermal efficiencies, often only a few percent, are thus that the theoretical separation energy is for work rather than thermal energy and because every process in the separation system needs a driving force, whereas the theoretical figure is based on reversible processes with no driving force. A practical process must create sufficient driving forces in the form of concentration, pressure, temperature or chemical potential gradients. Furthermore, to achieve a practical size of equipment large gradients are needed and energy and material flows over such gradients incur significant energy and hence efficiency losses.

A simple illustration of the obstacles to achieving energy efficiency for separation close to the theoretical would be the use of a membrane for separation of CO_2 from flue-gas. Theoretically a compressor could draw the CO_2 through a perfectly selective membrane. The first practical problem is that if all the CO_2 was to be recovered, the suction pressure would need to be zero and the compressor would be infinitely large. Thus a set of membranes each connected to a compressor of successively lower suction pressure could be used with a limit to the lowest pressures so that only say 90% of the CO_2 is recovered. What at first sight might seem a simple and efficient process has a significant limitation to the recovery efficiency. For a typical coal-fired power station flue-gas, containing 14% CO_2, this compromise of 90% recovery would need a highest compressor suction pressure of 0.14 bar absolute and a lowest of 0.014 bar absolute. Furthermore, to reach the minimum separation work each compressor would have to be isothermal, thus consisting of many small stages with inter-cooling. Lower pressure stages could however feed into higher pressure stages, limiting the amount of machinery required to some extent. In practice there would also be a resistance across the membrane so that the compressors would have to operate at pressures somewhat below the partial pressure of CO_2 on the other side of the membrane thus increasing their power requirement. Reducing the differential would reduce the power but would require increased membrane area so that a practical balance has to be struck. Dividing the system into more than several stages would entail an over-complex plant and these practical limitations to how "work" can be applied to perform a gas separation underlie the low efficiencies of the many different types of processes which can be used. This example illustrates the many practical barriers to performing gas separations with energy inputs approaching anywhere near to the theoretical minimum.

Examination of the combination of power production and CO_2 separation processes shows that there are synergies between the power production and gas separation tasks which can be exploited to reduce costs and increase thermal efficiency. Further synergies are to be found between the gas separation task and other major process industries. Examples in power production are the use of combustion air as a sweep gas in membrane separation processes, and the use of steam both as a working fluid and a chemical reagent in the fuel conversion process. Examples in wider industry are use of LNG for CO_2 condensation or anti-sublimation, use of calcium oxide/carbonate for CO_2 removal and as a constituent in cement clinker manufacture.

2.8.3. Relationship between energy consumption for capture and costs

Addition of a capture process will add a number of unit operations each of which will require input either of work or thermal energy. Each unit operation will reject some or all of the input energy as heat at a lower temperature than supplied. This rejected heat is available for conversion to work and hence electrical energy if it is at a high enough temperature. In some cases (e.g. turbo expansion processes) work input in one operation (e.g. compression) can be recovered as work in a subsequent process (e.g. turbo-expansion). The additional generating capacity which has to be added to maintain net power output when a capture process is added will be the amount of work consumed as a result of the addition less the amount of work which can be recovered by using the heat or power rejected by the capture processes. Note that part of the additional work is needed to increase the capacity of the normal power plant auxiliaries. This defines the increase in the size of the generation unit and driver.

The additional fuel which has to be consumed is in part due to that required to generate the extra power. However, where heat is consumed by processes this will require an additional amount of fuel. This amount of additional fuel is determined by the amount of heat but is reduced if the heat is rejected at a temperature high enough to be used in the power generation process and has an appropriate destination. Heat at or above the saturation temperature of steam at the LP turbine inlet pressure has such a destination but below this temperature the main destination is feed water heating for which there is strictly limited capacity. The reduction is in the ratio of the amount of heat multiplied by the efficiency which corresponds to its temperature or the maximum utilisable temperature in the process whichever is the lower. A consequence of this is that heat consumed and then rejected while still above the maximum temperature useable in a steam raising coal plant of around 650ºC would not in theory require any additional fuel to be consumed. The heat flowing through the process would thus effectively be free. Again, where extra fuel has to be consumed this is further increased by any auxiliary power consumed by those units whose capacity is primarily set by fuel flow.

In most capture processes a significant element is compression of CO_2 and it is thus possible to subdivide the additions for capture into the compression element and the rest of the processes. CO_2 compression is a consumer of work, some of which is rejected as heat that can partly be recovered and converted back to work. In assessing the potential efficiency of a capture process the recovery of rejected heat needs to be taken into account and in order to make a balanced comparison the same cut-off criteria for implementing heat recovery need to be applied.

In order to make comparative estimates of cost it is useful to identify by how much the thermal capacity and the electrical capacity of the plant needs to be augmented to provide the energy inputs needed by the capture processes. Analysis of the work and thermal requirements along with their heat rejection characteristics enables this to be estimated and this approach will be used wherever possible in making comparison of the cost of electricity. Furthermore it would also be useful to be able to attribute costs for increasing the size of elements in the base plant to the different elements of a capture process in order to assess the scope for cost reduction.

NETL has produced a suite of studies which contain detailed estimates, using a consistent methodology, covering post-, pre- and oxy-combustion capture processes [NETL 2008, NETL 2010, NETL 2012, NETL 2013]. Analysis of the detailed capital cost estimate [NETL 2012] prepared for the Fluor Econamine FG Plus process has been performed to identify the contributions which consumption of extra fuel and power make to the cost of electricity. This shows that consumption of extra fuel and power accounts for about 37% of the increase in LCOE whilst the remaining 63% is attributable to the additional capture equipment. It also shows that there is a slightly higher LCOE penalty for utilising extra power. A 1% increase in fuel consumption to provide thermal energy results in a base plant LCOE increase of 0.82%, whereas for the same percentage increase in power consumption a 0.95% increase in base LCOE results. It is slightly higher because the electrical power generation components have to be larger. Note that these are percentage increases. Where electrical power is consumed by the capture process instead of thermal energy, the absolute consumption of fuel increases far more due to the inefficiency of the process converting thermal energy to electrical energy. For the purposes of comparative evaluation in this study a thermal to AC electrical energy conversion efficiency of 40% has been used when no other value is available.

2.8.4. Costs – Conventional post-combustion capture

The extra cost of producing electricity for a plant fitted with conventional post-combustion capture technology is made up of two main elements. Using the recent NETL 2012 study as reference, the additional costs of electricity are attributed to an 88% increase in the capital element and a 52% increase in the operating cost element. However, the capital element is reported at a slightly higher value than the basic 76% increase in overnight capital cost as higher risk factors are used in calculating the cost of capital. For strict comparison purposes the capital element should be adjusted downwards accordingly to respect the NOAK estimating basis. The estimate recognises 12 relevant subsections, 7 of which are closely related to thermal capacity, one to gross electric power output, one to cooling water (CW) load and 4 are more general categories which are affected by a variety of factors. It thus allows the effect of the changes in thermal and electrical loads introduced by adding capture to be linked directly and proportionately to capital costs. For evaluation of other post-combustion type technologies the same factors will be used for estimating how capital costs will change.

The assessment of variable cost differences is somewhat easier. Standard prices for fuel and key process materials such as limestone sorbent will be used. An element of the fixed costs will be presumed as being proportional to the capital cost using a suitable percentage.

The other factorial adjustments which need to be made are for cost of capital and year of estimate. Capital charge will be based on total overnight cost escalated to 2014, converted where necessary to US$ to which a fixed factor will be applied representing a 30 year lifetime, low risk financing route as adopted for the base power plant in the NETL study of post combustion capture technologies [NETL 2012]. LCOE is a factor 1.47 higher than COE due to the effects of the inflation assumptions which are assumed to be zero for the LCOE calculation. The uplift from the 2007 baseline to 2014 based on the CEPCI index is a factor 1.08.

CO_2 removal from flue gas by absorption in an amine based solvent process is one of the leading technologies for post combustion capture (PCC). There has been continuous research effort to reduce the energy penalty and cost of CO_2 avoidance for the CO_2 absorption process. The research work undertaken has focused on improvements in solvent characteristics, modifications to the process flow scheme and heat integration.

3. Post combustion capture

3.1. Improvements to amine solvent absorption

Regarding solvent development, different amine based solvents have been developed such as precipitating 2-Amino-2-methyl-1-propanol (AMP) + carbonate solvent process; activators such as Piperazine and Triethylenetetramine have been used to improve the absorption rate for existing solvents such as Monoethanolamine, 2-amino-2-methyl-1-propanol, Diethanolamine etc. The focus for these newly developed solvents is on improving the CO_2 absorption rate, absorption capacity and heat of regeneration. It is also important to focus on developing fundamental data such as: vapour liquid equilibrium, absorption rate constant, enthalpy of absorption and heat capacity for newly developed solvents at real process conditions and especially at the stripper conditions (~120°C and ~1.5 Bara) (see Figure 5).

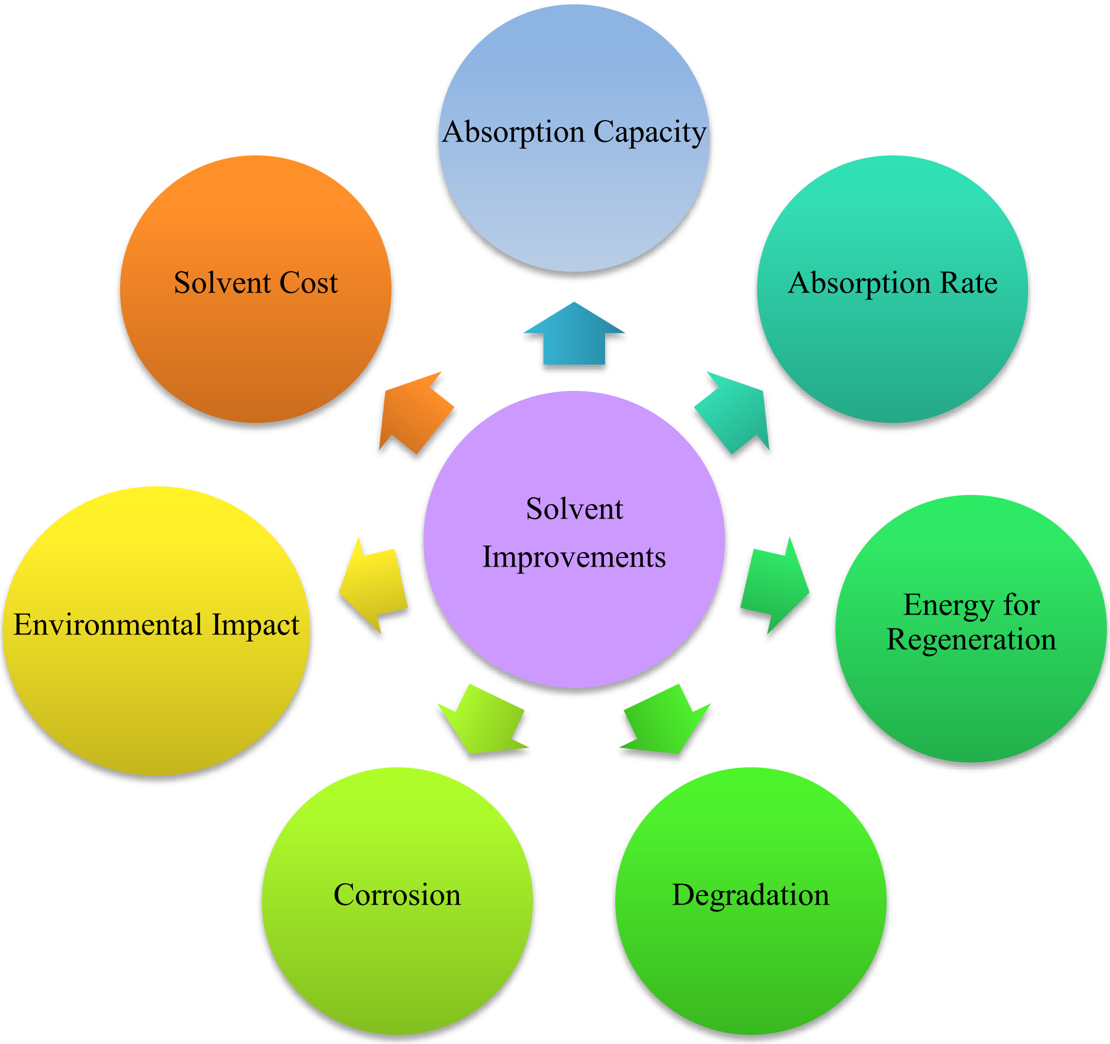


Figure 5 Important factors to be considered when developing a solvent for CO_2 absorption process.

With regard to process improvements, various process modifications have been proposed in the literature such as: Split flow process, Heat pump distillation with a Split flow process, Absorber Intercooling, Matrix stripping, Multi stage stripping, Lean Vapour recompression etc. Currently the evaluation of these process improvements focuses mainly on the energy requirement for the CO_2 capture plant and for conventional amine based solvent (Monoethanolamine). However, it is also important to focus on evaluating these process improvements on the basis of the process economics as well as for improved solvents. Currently IEAGHG is looking into these different process modifications on the technical and economical basis for coal and natural gas based power plant. Moreover, in the current state of power plant operation, it is also important to evaluate these process improvements on the basis of plant dynamics and process control during full and part load conditions. IEAGHG has in undertaking a project on developing process control strategies for different operating conditions for post combustion capture processes at coal and natural gas based power plant.

The environmental impact of the amine based CO_2 absorption process is an important area to be further understood. In order to avoid amine emissions to the atmosphere, it is important first to develop an understanding of different amine based solvent degradation rates under real process conditions. Further, it is also important to develop suitable emission monitoring technologies such as Fourier transform infrared spectroscopy (FTIR). Aerosols can be present in the treated gas leaving the absorber, which can be reduced by having suitable plant operational conditions such as water wash temperature control to minimise aerosol emissions. Further evaluation of flue gas filters and their effectiveness in avoiding aerosol emissions needs to be performed. Moreover, other options such as an acid wash on top of the absorber, maintaining a suitable acid wash liquid pH and salt concentration can also be an effective method to reduce emission of other alkaline components (e.g. MEA, degradation products, etc.) Another suitable emission reducing technology demonstrated at pilot plant scale is to have an adsorption bed above the absorber, which will require no additional liquid stream; no waste stream generated and will have very little pressure drop. This adsorption bed technology has been tested successfully at RWE Pilot plant Niederaussem, Germany. A recent IEAGHG study on ‘Evaluation of reclaimer sludge disposal from Post Combustion CO_2 capture’ looked into different reclaiming technologies such as; thermal reclaiming, ion exchange and electrodialysis for conventional solvents on the basis of their technical and economic performance. Furthermore different reclaimer waste disposal options such as landfilling, co-firing in a boiler, using in a cement kiln and waste water treatment were also evaluated.

Currently there are several solvent based pilot plant and demonstration projects in operation/construction/planning around the world. These pilot plant operations based on different post combustion technologies have successfully demonstrated the applicability of the amine based solvent CO_2 absorption process. These pilot plants have identified improvements in the technology which will result in reducing both the capital and operational costs. Also, from these pilot plants robust procedures, operating guarantees and competitive performance have been developed. These pilot plant tests have provided invaluable knowledge for incorporation into the full commercial deployment of PCC technology.

In addition to the process modification and improved amine solvent described above, various novel technologies are being researched to improve the efficiency, environmental performance and costs of post combustion capture. The main technologies are described below and their environmental impacts, energy consumptions, material/solvent costs and costs of CO_2 avoidance compared to current solvent scrubbing technology are summarised in tabular form at the end of this section of the report.

3.1.1. Cost reduction potential of improved solvents

Fig 5 identifies 7 areas of improvement for conventional capture and in this section an estimate of the potential for reduction of LCOE through each type of improvement will be made and the particular elements of the LCOE which are likely to be affected will be identified. Some of the areas are closely interrelated and this interdependency will also be discussed.

The provision of the thermal energy for regeneration causes increases in the coal receiving and handling facilities, the boiler, feedwater system, flue gas clean up and ash/spent sorbent handling systems more or less in proportion. Generating capacity is not directly affected and other systems will only increase in cost to a minor extent. This element of the base plant represents 67% of the capital cost. Compression power and additional power for the induced draft fan and solvent circulation pumps are the main additional electrical auxiliary loads. The turbine/power generator represents only 13% of the total cost and also has to increase when energy to the capture process is supplied as work. Cooling water systems represent only 4% of the cost and other systems such as instrumentation, general electrical distribution and buildings are the final 16%. Cooling water can be considerably increased if the process rejects a lot more low grade heat but the other elements are less affected by fuel or power increases.

When the fuel or electric power systems are increased in capacity their associated electrical loads also increase so there is a small multiplying effect. In the base plant the electric auxiliaries are 5.2% of the gross power so for every 10% increase in power for the capture process a further approximately 0.5% is required to provide for the increase in these.

Analysis of the NETL 2012 estimate reveals that the additional thermal and electrical loads require a 38% increase in fuel and a 14% increase in total power. The increase in auxiliary power can be divided into three elements: compression power, power for and directly related to the Econamine FG Plus process (e.g. extra power for the induced draft fan to overcome pressure drop) and finally additional power related to the increase in thermal energy for the Econamine FG Plus process. The calculated division is shown in table 5 below.

Table 5 Typical breakdown of parasitic energy requirements for solvent based PCC

User of extra auxiliary power	**% of extra auxiliary power**
CO_2 compression	42% of which 2% indirect
Econamine related electrical power	24% of which 1.2% indirect
Econamine related thermal energy	34% all indirect

The 38% extra fuel is partly for generating the extra power for compression and the Econamine FG Plus process (14%) and partly for providing additional thermal energy for solvent regeneration (24%). Overall the approximate division is that 42% of the 14% extra fuel for extra auxiliary power is for CO_2 Compression i.e. about 5.9%. The Econamine FG Plus process demands 24% more fuel for its thermal requirement and 58% of the 14% i.e. 8.1% more for the extra power demands. These factors can be used to give some insight into the potential cost reductions which solvent improvements could offer. They are based on the cost breakdown used by NETL and other analyses may produce slightly different breakdowns.

Apart from those elements of cost directly associated with either fuel rate or power there are 5 other more general elements each of which increases primarily as a result of these increases but also as a result of addition of the capture process. To estimate the effects of the additional fuel and power these costs also need to be allocated.

Before doing this an adjustment is made to reflect the fact that the estimate made by NETL is for a larger gross capacity and beneficial scaling effects have been taken into account. The adjustment is made by factoring each of the base plant cost elements up to reflect their true percentage capacity increase. The capture plant cost is then escalated with an exponential scaling factor of 0.75. The unit costs per MW are then in line with what those of a 550MW gross plant with capture would be.

The costs of the 5 general systems are firstly split between costs for the capture plant and costs for the fuel and power capacity increase. A basis for this first split could be the ratio of additional base plant costs to new capture plant costs which in the adjusted NETL estimate is roughly 39:61. Within the assumed 39% contribution of these systems to the base plant cost increase a further split in the ratio 13:67 between power generating cost increase and fuel related cost increase is made (i.e. 16% and 84%).

This translation into the effects on the capital and hence capital charge element of LCOE results in the split summarised in Table 6 and Figure 6 below.

Table 6 Contributions to increased LCOE of main users of parasitic energy in solvent based PCC

Element	Contribution to 38% Extra Fuel	Share of Extra power contribution	Extra fuel cost contribution	Extra power cost contribution	Total contribution
CO_2 Compression	5.9%	42%	13.0%	6.7%	19.8%
Econamine FG plus related electrical power	8.1%	24%	17.9%	3.8%	21.7%
Econamine FG plus related thermal energy	24%	34%	53.1%	5.4%	58.5%

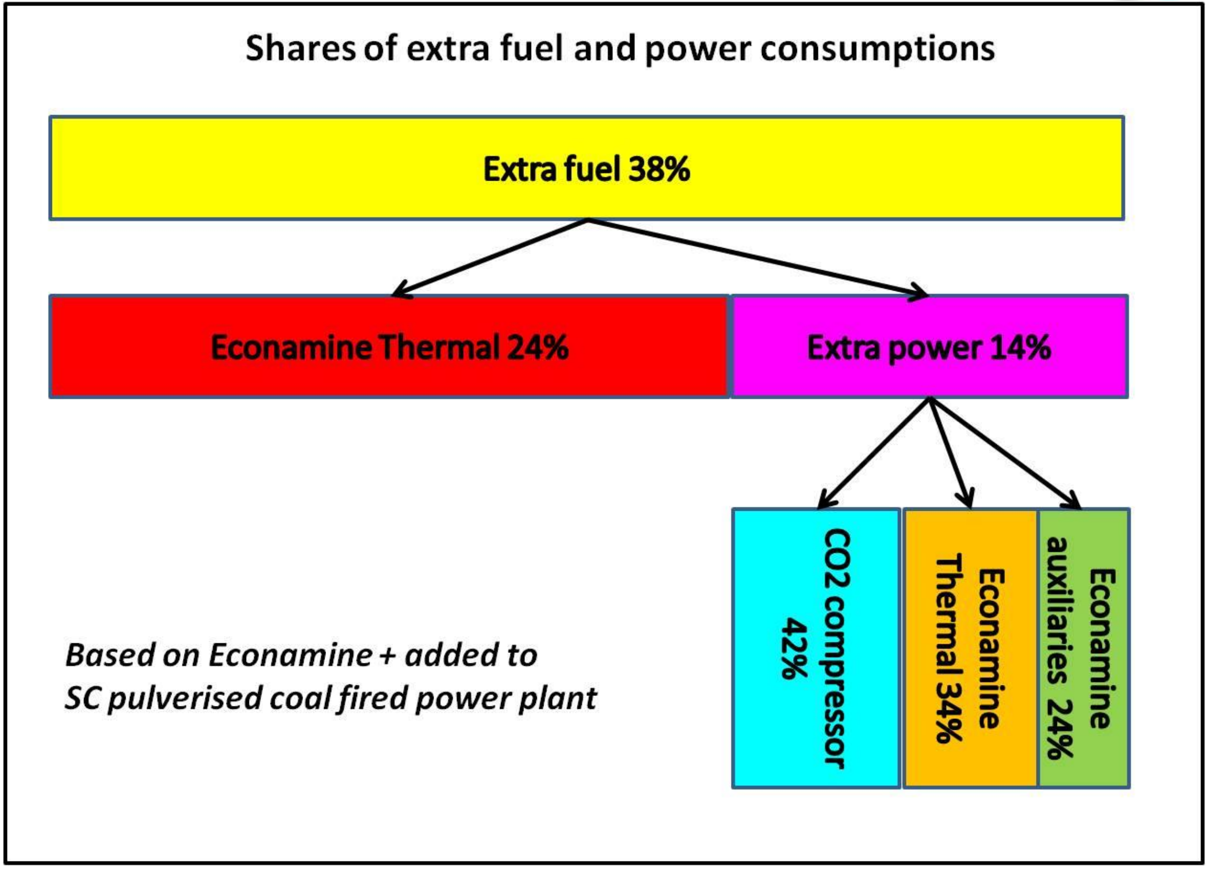


Fig 6 Split of contributions to extra fuel and power in typical solvent based PCC

The capital increase works out to be almost exactly 33% due to increases in the base plant cost and 67 % due to the additional capture equipment. Thus 33% of the total cost increase can then be apportioned in the ratio 19.8:15.7:58.5 between the compression, capture electrical auxiliary increase and capture thermal load respectively. In considering the effects of improvements to the solvent capture process it is thus possible to say which elements of overall LCOE would be targeted by particular innovations.

The capital charge element of LCOE for post combustion capture using solvents is not the only element affected. Also the fuel cost and variable and fixed costs will all be increased to a greater or lesser extent. Fuel cost will increase in proportion to the extra fuel contribution tabled above. The variable costs increase partly because of the increased cost of consumables used by the main power process and partly because of those used by the capture process. A proportion of the variable costs is maintenance materials which are related in some proportion to the total capital cost. In the NETL estimate this capital related element is 0.8% per year of the total overnight capital. The estimate also indicates the proportion of variable costs which are incurred by consumption of more chemicals in the main power process allowing those solely for the capture plant to be separated. This gives a benchmark for the split of these contributions to the LCOE and hence identifies the potential for cost reductions by different types of process improvement.

The fixed costs in the NETL estimate are based on assessment of the labour requirements and are thus not necessarily related to capture plant cost or efficiency. They also include an amount for taxes and insurance which is equal to about 1.6% per year of the capital. Hence in total the operating costs include about 2.4% per year of the total capital. These parameters can be used to give an estimate of the effect which solvent improvements might have on cost of electricity. Thus when total capital increases there is an associated element of operating cost increase which for the NETL estimate amounts to a further 20% of the capital charge.

The apportionment of the extra operating costs to LCOE are shown in figure 7 below. Percentages are based on the NETL cost estimates adjusted to reflect plants of equal gross power output and low risk Nth of a kind financing. The figures are rounded off and will be used as part of the benchmark for evaluating cost reduction potential. It should be borne in mind that this is just one benchmark estimate and others may result in slightly different apportionment.

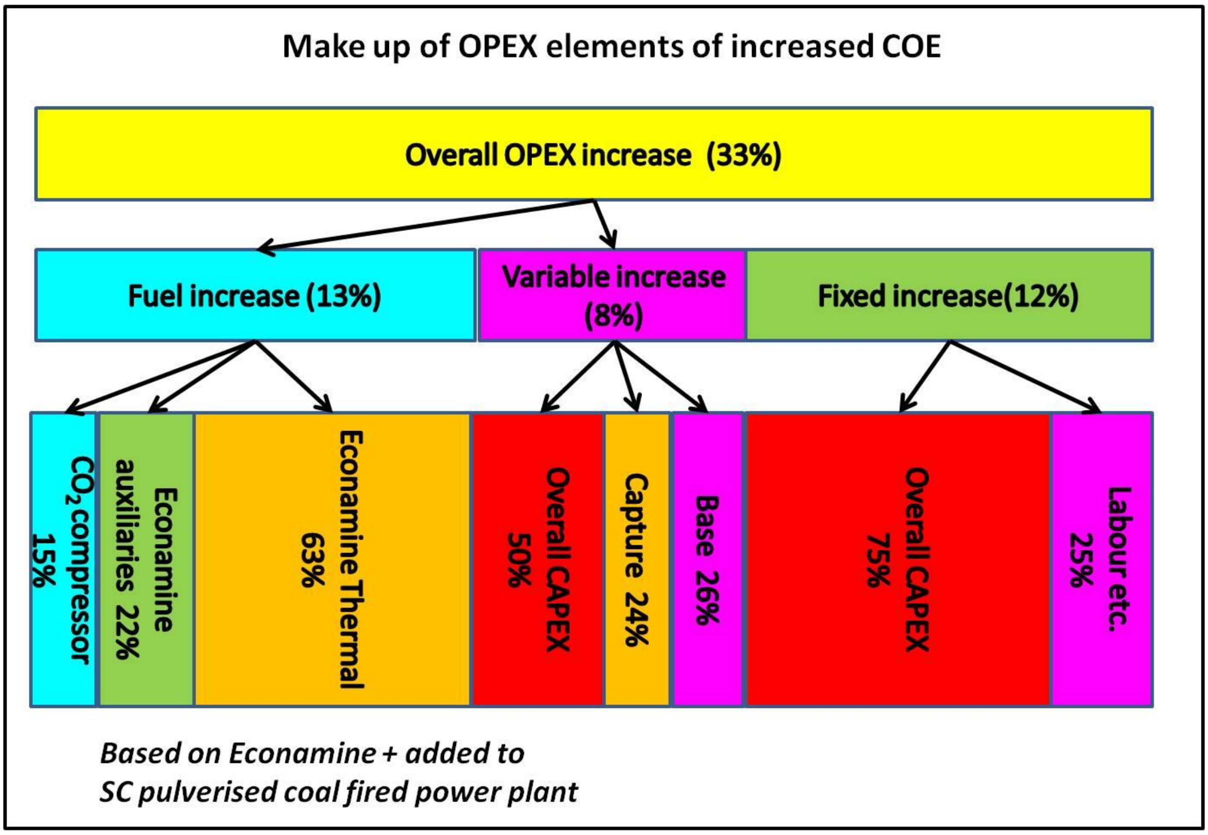


Figure 7 Split of contributions to additional OPEX in typical solvent based PCC

Reductions in regeneration energy will reduce fuel costs, the capital charge element associated with extra fuel consumption, and parts of the variable operating costs which are dependent on the fuel consumption or fuel consumption related capital cost. From this analysis the all-pervasive effects of increased energy consumption on the capital and operating costs of producing electricity are evident. Using the above factors the effect for example of a 1% change in the thermal energy requirement of the power plant (i.e. the fuel consumption) on overall LCOE increase can be calculated. This works out to be just 0.47% and helps illustrate what the potential for different types of improvement in solvent performance will offer.

3.1.2. Thermodynamic and chemical equilibrium considerations

The absorption of CO_2 into a reactive solvent is a chemical reaction and there is an equilibrium loading which depends on the free energy of the CO_2 solvent reaction. The higher the free energy of reaction the greater the solvent loading. The enthalpy and free energy of reaction are usually similar and thus the heat required to decompose the rich solvent is depends roughly on the free energy of the reaction. When the free energy is low the amount of CO_2 which can be taken up at equilibrium is also low so that much higher solvent recirculation rates are needed to remove the same amount of CO_2. Whilst the heat for decomposing the rich solvent goes down that for providing the sensible heat to warm the solvent to regeneration temperature goes up. A substantial amount but by no means all of this sensible heat is recovered by heat exchange. There is thus an optimum heat of reaction where the total heat of regeneration is minimised. This is estimated to be around 77kJ/mol which is only slightly lower than that of MEA. A goal of low heat of reaction solvent alone does not minimise regeneration energy. Higher solvent loading can be achieved by having higher concentrations of the active species or by selecting lower molecular weight reagents. These will both reduce the sensible heat losses from warming and re-cooling the solvent. Typically the heat requirements are split roughly equally between three components, the heat for decomposition, the sensible heat loss and the distillation loss which is incurred when steam or other vapour is produced in the regenerator reboiler and subsequently condensed at much lower temperature in the condenser.

A further consideration is that because of chemical equilibrium effects the temperature required for absorption reduces as the heat of reaction decreases to the point that refrigeration may be required. These theoretical thermodynamic and equilibrium effects are described by [van Nierop et al. 2011] and figure 8 below illustrates the effect of reaction enthalpy on operating temperatures. This will be a consideration when considering for example precipitating or demixing solvents. These enable significantly higher CO_2 loading so that the optimal solvent may have a lower free energy of absorption. However if reduced too far there could be a refrigeration energy penalty. On the other hand the efficiency and economic effects of this could be offset by the accompanying lower regeneration temperature which may enable normally unused low grade heat sources to be applied.

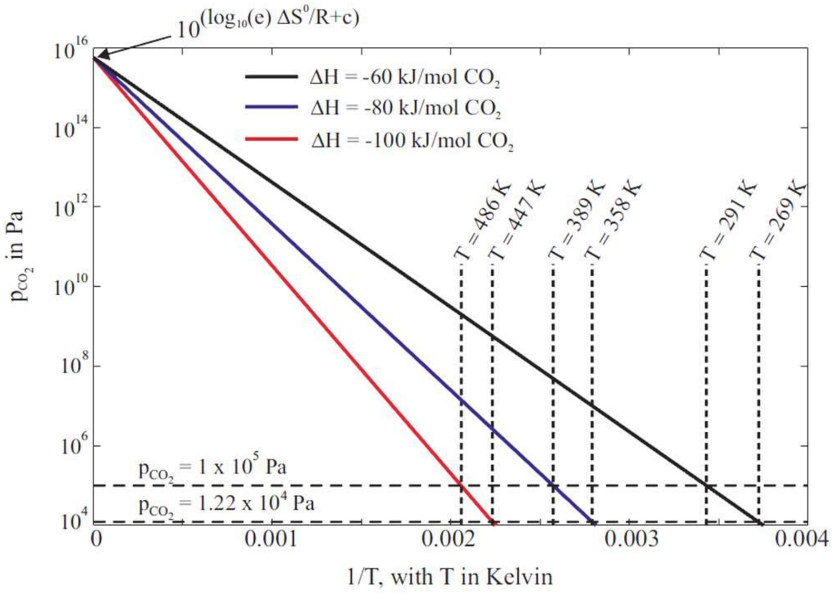


FIG. 2. Partial pressure of CO_2 over an amine solution with different ΔH. The required temperatures in the absorber and stripper are set by ΔH and the required operating pressures (which are assumed to be equal to the equilibrium p_{CO_2}).

Source . Effect of absorption enthalpy on temperature-swing CO2 separation process performance .E van Nierop et al. Energy Procedia 4 (2011) 1783–1790

Figure 8 Relationship between ΔH and CO_2 solvent absorption/regeneration temperatures

3.1.3. Solvent processes with lower heat of regeneration

Research in this area can best be assessed on the basis of the overall reduction in process heat requirements rather than on the basis of heat of reaction of CO_2 with the absorbing species. Solvents have already been developed which are close to the optimum free energy of reaction so that formulations which allow higher loading through increases in concentration of active species, lower sensible heat capacity of solvent per unit active species or closer approach to equilibrium in the absorber are the most likely to help reduce energy consumption. Improvements to the process by improving heat recovery and use of vapour recompression schemes are also potential routes to lower energy consumption. All of these approaches are likely to produce only incremental performance improvements but they do have a significant effect on LCOE.

3.1.4. Solvents with higher absorption capacity

This approach is closely related to the more general approach of researching for solvents with lower regeneration energy. It principally targets the sensible heat loss which represents about 1/3 of the thermal energy consumption of the baseline process. However care needs to be taken that other key solvent properties are not changed adversely. In particular higher concentrations often result in more viscous solvents with poorer mass transfer properties. This would reduce approach to equilibrium or require a larger absorber to compensate, both of which would tend to reduce the cost advantages. Assessment should thus always be based on the expected overall process efficiency.

3.1.5. Solvents with higher absorption rate

The chemical and physical driving forces for absorption are quite low so that the absorber column has to be large and hence is costly. The CO_2 has to overcome mass transfer limitations to enter the solution from the gaseous phase and also chemical reaction limitations to become dissolved as reactive ions before it can react with the absorbing species. The results are that full equilibrium may not be reached at the bottom of the absorber thus reducing solvent loading and larger absorption columns. Research into methods of improving absorption rate can thus directly reduce capital costs and in general are not counterbalanced by other negative effects on efficiency.

3.1.6. Solvents with lower degradation rates

Solvents degrade through reactions with acid species in the flue gas such as SO_2 and NOx. They also degrade through chemical side reactions. They also degrade thermally with the highest rates experienced in the regenerator reboiler where temperatures are highest. The degradation has three main effects. The concentration of active species reduces and thus the degradation products have to be removed and solvent replaced. By products may form which accelerate corrosion. Thirdly the rate of thermal degradation increases with temperature thereby limiting the acceptable temperature in the regenerator. This has a small knock on effect on the CO_2 compression power as operating at higher pressure, which requires higher temperature, reduces the required compression ratio to reach export conditions. Developments which reduce degradation will thus have a small effect on solvent replenishment costs, cost of corrosion inhibitors and may allow some cost reductions in the CO_2 compression system which will include those associated with reduced power.

3.1.7. Solvents with less corrosive properties

As CO_2 is present with water in solvent systems which use aqueous formulations there is potential for acid corrosion in parts where acid conditions exist. Parts of the process operate under alkaline conditions because of the basic nature of the solvents. Thus corrosion resistant materials are specified for significant parts of the capture plant which range from use of stainless steel either solid or as cladding and corrosion resistant tiles or polymeric linings. In addition corrosion inhibitors may be added to limit corrosion. Corrosion caused by degradation products is a complex issue because the concentration of these can build up over a long time. Improvements in this area will thus have a second order effect on LCOE potentially through cheaper equipment by allowing use of cheaper materials of construction, through lower costs of solvent replacement and inhibition chemicals. Corrosion repairs may also be reduced although this cost is not explicit in cost estimates.

3.1.8. Lower cost solvents

Solvent consumption as a result of degradation, operational leakages and to atmosphere or to stack clean up system represents a small but significant on-going cost. If the solvent is expensive then the costs for initial fill also become more significant. Higher performing solvents on the market are more expensive partly because they contain more expensive compounds but also because they are sold through proprietary process licensors who need to recover development costs. An example of a very cheap solvent is ammonia. So one aspect of developing low cost solvents is to be able to make use of such low cost bulk chemicals in a practical process. The conventional solvents such as MEA are also relatively cheap compared to higher performing solvents such as Mitsubishi’s KS series. Enabling the low cost solvent options to perform better is thus potentially worthwhile developing although the cost benefit in terms of overall LCOE will be limited. High performing, high purchase cost solvents which exhibit very low losses through degradation or evaporation are another interpretation of “low cost”. Such developments are also worthwhile if accompanied by over-riding energy performance improvements.

3.1.9. Improved solvents - Current status and technology readiness level

Facilities are available to test the performance of new solvent formulations at significant scale. If satisfactory tests have been carried out in such a large scale facility, the technology readiness level would be at TRL-6. Change out of solvent would also be possible at the first full scale capture units which are now coming on line and successful demonstration in such a facility would reflect TRL-7 and if proven in a facility of >100MW then TRL-8

3.1.10. Overall efficiency and cost prospects for improved solvents

IEAGHG has evaluated the effects of a range of improvements to the conventional solvent process. These included presumed improvements in solvent performance (termed “Solvent 2020”) enabling stripper operating pressures to be raised as high as 5 barg. Other improvements were process improvements including addition of intercooling for the absorber and heat recovery from compression and regenerator overheads. Whilst improved solvent can be a significant contributor to efficiency reduction the various process improvements are also key contributors. Analysis of the effects on LCOE showed that effects of process improvements were small and sometimes negative because increased capital cost sometimes outweighs any reduction in operating cost. The results are shown in figure 9.

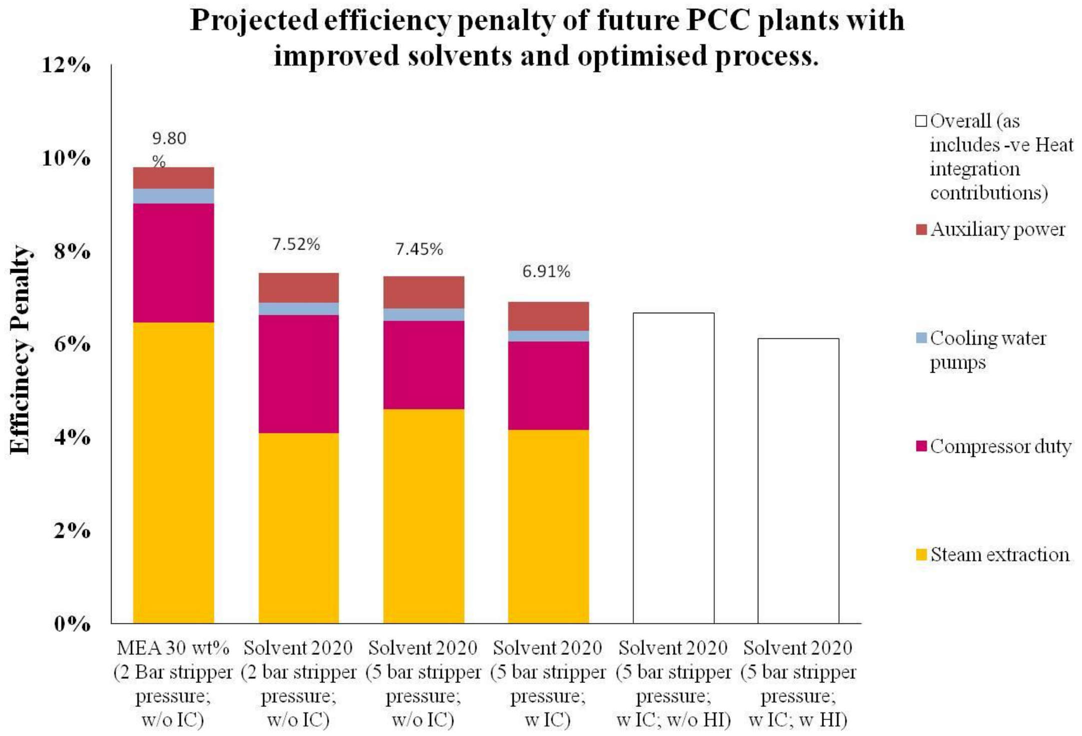


Figure 9 Projected efficiency penalty of future PCC plants with improved solvents and optimised process

3.2. Encapsulated Solvent

A new concept is to use an encapsulated form of carbon capture solvent in which the operating fluid, amines or carbonates is enclosed in a thin polymer shell forming 200-400 μm beads. These beads are intended to dramatically increase the surface area of solvent in contact with flue gas as alveoli do in mammalian lungs (see Figure 10).

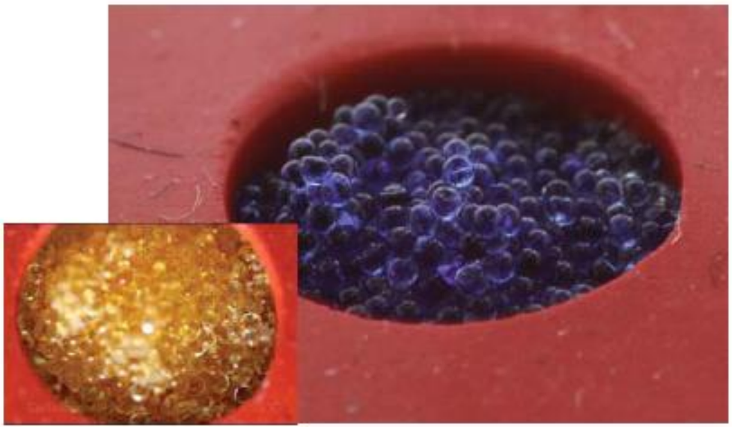


Figure 10 Carbonate-filled capsules with thymol blue as a pH indicator (inset shows loaded capsules) [Aines et al. 2013]

In order to provide this functionality, the polymer shell must be highly permeable to carbon dioxide, permitting the inner solvent to perform the selectivity role, but it must also be strong enough to survive an industrial regime in which capture, and presumably release of pure CO_2 via heating, occurs over thousands of cycles. Several carbon dioxide capture solvents of interest, including MEA, piperazine, sodium carbonate, and potassium carbonate, at concentrations up to 30 wt. % have been encapsulated. Silicones and NOA (Norton Optical Adhesive) as the polymer material is used for encapsulation. In all these systems the liquid remains immobilized within the polymer capsule while gas is absorbed through the shell. The capsules may then be heated to release the captured CO_2. Encapsulated solvents have the capacity of liquids and the physical behaviour of solid sorbents. It is assumed that these encapsulated solvents will be useful in fairly conventional-style capture applications, as well as exotic new approaches facilitated by their high surface area. The liquid, as well as any degradation products or precipitates, remains encapsulated within the beads.

3.2.1. Cost reduction potential of encapsulated solvents

The key areas for potential cost reduction will be in the heat and power consumption as compared to conventional systems and in reduction in the size and hence cost of equipment. Encapsulation may also allow higher temperature/pressure regeneration with associated reduction in CO_2 compression requirements. There would be two main options for the process, either use of fixed beds or circulating fluid beds. Scale considerations would suggest that circulating beds would be more appropriate for large power plants. The arrangements for regeneration on a large scale need some consideration. The carrier for introducing heat and that for removing the CO_2 released need to be selected. Steam and CO_2 are the obvious choices if a gas is used as heat carrier. Consideration also has to be given to whether and how heat supplied for regeneration will be recovered. In a liquid system this can be done in a heat exchanger without any intermediate fluid. In a solid system it is likely that an intermediate fluid would have to be used. Another consideration in the cycle is the water balance since the regeneration tests using dry nitrogen revealed that water is lost and the surface of the capsules wrinkles. This dry out was however observed to be reversible. Nevertheless a cycle, which maintains the water balance of the capsules, may be advantageous indicating that steam, rather than dry CO_2 might be a preferred heat carrier gas.

At this stage the research has not addressed how the capsules would be used in a large scale practical process.

3.2.2. Thermodynamic considerations

The researchers point out that using capsules the problems of high viscosity of concentrated solvents and its effect on mass transfer is much reduced. This would thus allow much higher solvent loadings to be achieved, which in a conventional process would allow the sensible heat loss to be reduced. However unless a process which allows the same level of heat recovery is found this advantage cannot be exploited. The other loss which will be affected is the distillation loss. If steam is used as the regenerant gas the system will behave as though live steam is being used. This will assist in lowering the partial pressure of CO_2 to a greater extent than a system with indirect heating of the solvent potentially reducing the distillation loss. In a system with circulating CO_2 as regeneration gas heat would be supplied indirectly to the CO_2. Any water which evaporates from the capsules would represent an additional energy loss akin to the distillation loss in a conventional solvent system. However if encapsulation allows very low or even water free solvents to be used this would be eliminated.

In summary the use of encapsulation opens up possibilities to greatly reduce some of the inherent energy consumption of conventional solvent systems but does depend on how the loss of an easy sensible heat recovery method counterbalances this advantage. The revised balance between heat of absorption, sensible heat and distillation loss components may shift the optimum free energy of reaction to a lower level. To evaluate the possible potential of encapsulated solvents suitable processes using the technology need to be designed and simulated.

3.2.3. Current Status, technology readiness level and development requirements.

As part of a US-DOE ARPA-E program, a team from the University of Illinois Urbana-Champaign, Babcock and Wilcox, and Lawrence Livermore National Laboratory has created a new encapsulated form of carbon capture solvents in which the operating fluid, amines or carbonates in the tests to date, is enclosed in a thin polymer shell forming 200-400 μm beads. Aines et al. 2013 have demonstrated rapid CO_2 uptake and desorption using colorimetric methods, which permit rapid spectroscopic determination of the extent of CO_2 uptake and release. Results from this study showed the mechanical/thermal cycling tests demonstrate long-term stability of silicone encapsulated carbonate.

First experiments on encapsulated solvents have indicated some potential. It is too early to formulate a full application until more has been done to characterise and optimise capsule performance. The technology readiness level is therefore assessed as TRL-1.

Further testing under real flue gas condition needs to be performed and pilot plant tests are required in order to develop better understanding of this type of solvent. HSE related issues such as solvent handling and environmental impact of these encapsulated solvents also need to be looked at in further detail and cost benefits reported.

3.3. Precipitating Solvent

Certain solvents such as inorganic solvents (potassium carbonate) and amino acid salts tend to precipitate (i.e. solid phase) when they react with CO_2. This precipitation is to be avoided in conventional process configurations but by doing modifications precipitation can be used to create a highly concentrated CO_2-rich phase (slurry). This concentrated slurry is then sent for regeneration, while the solvent is sent for further CO_2 absorption (see Figure 11). However it is important to consider that in these type of solvents the majority of CO_2 is converted into the precipitate.

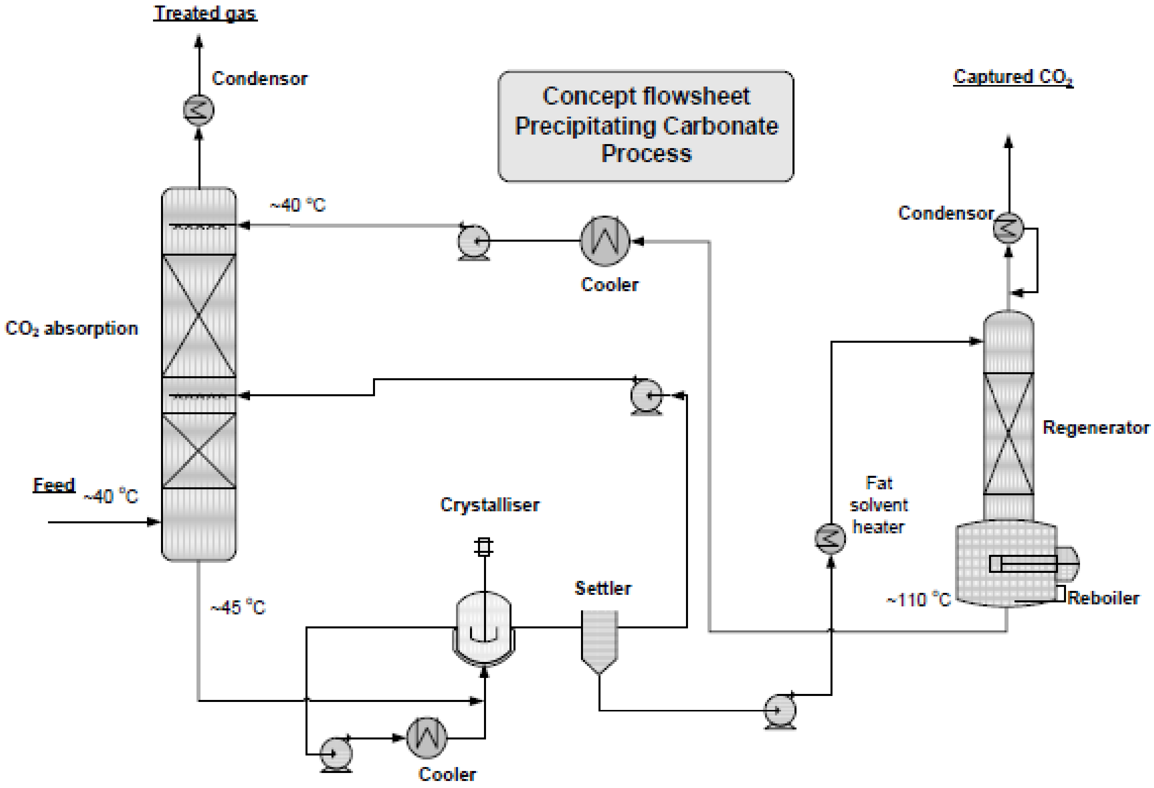


Figure 11 Shell Global Solutions carbonate slurry bench-scale pilot-plant [Moene et al. 2012]

This precipitating solvent allows a lower energy requirement for solvent regeneration and also it is possible to regenerate at higher pressure, which will result in energy savings from CO_2 compression. These solvents also tend to show low degradation. Moreover this technology shows low cost and is based on well-known separation principles. Regarding to the environmental impact the inorganic solvent will have lower impact but when using the ammonia process further related HSE must be evaluated.

3.3.1. Energy requirement / Cost evaluation

The amino acid salt based DECAB process from TNO has been evaluated based on coal fired power plant flue gas conditions with 90% CO_2 capture rate [Feron et al 2005]. The reported energy requirement for the DECAB process was 2.34 GJ/tonne CO_2 compared to conventional amine based solvent Monoethanolamine (MEA) which was reported to be 4.2 GJ/tonne CO_2. A more recent paper [Fernandez et al 2011] reported 3.2 GJ/tonne with a possibility to reduce to 2.8 GJ/tonne if the residual heat in flue gas could be used for crystal melting prior to regeneration. This initially estimated reduction in thermal energy was substantial, representing a reduction to 55% of that for MEA. However the benchmark NETL study reported only 3.55 GJ/tonne so that the more recent evaluation suggests only a reduction to 90% with a possibility of increasing this to 79%. This would reduce the increase in COE by roughly 10 x 0.47 = 4.7% with a promise of a reduction to roughly 21*0.47 = approx. 10% when using the more recent NETL Econoamine FG Plus performance as a benchmark.

3.3.2. Thermodynamic and chemical equilibrium considerations

The attraction of precipitating processes is that the direct relationship between free energy of reaction and equilibrium concentration of products is broken. At the point that the CO_2 solvent product starts to precipitate its chemical potential ceases to rise as further CO_2 reacts. Thus the reaction can continue as any new product formed precipitates. The equilibrium relationship is no longer governing the loading. Instead the capability to slurry the solid product sufficiently for it to flow through the process becomes the limitation to solvent loading. This opens the way for lower free energy of reaction solvents to be used as well as allowing much higher CO_2 loadings to be reached.

3.3.3. Current Status, technology readiness level and development requirements.

Currently several precipitating solvents have been investigated by different companies and research organizations such as SINTEF/NTNU (Norway), TNO (The Netherlands), Shell Global Solutions, Alstom (Chilled Ammonia), University of Melbourne (Australia), CSIRO (Australia), CO2CRC (Australia). The activated potassium carbonate is the most mature system. This solvent has been tested at pilot/lab scale by Shell Global Solutions [Schoon et al 2011]. The University of Melbourne has tested CO2CRC's patented precipitating potassium carbonate concept at the pilot scale [Quyn et al 2012]. A chilled ammonia process (CAP) with precipitation has been tested by Alstom, but currently Alstom is operating their pilot plants without precipitation [Telikapalli et al 2012].

Precipitating solvents are still in the early developmental stage with the most advanced systems having undergone pilot scale testing. It is not clear to what extent all of the systems needed to handle solids has been proven in an integrated system and Alstom's limited progress in this area so far is possibly indicative of the need for further validation. Most of these systems are thus assessed as being at TRL-4 and those with some claimed pilot test results at TRL-5.

The next step will be to test this concept under real flue gas conditions at larger scale. For the chilled ammonia process the impact of SO_2 and NO_2 and required solvent reclaiming need to be further evaluated. Further research on the column packing materials and optimization of the liquid/gas ratio is required. It will also be necessary to establish the slurry concentration limits for transport through the piping, heat exchanger, circulating pumps and the column packings. In addition any tendency for solids to build up and slowly block the process will need to be checked by long pilot plant runs. If such tendencies are detected then practical methods for removing such build-ups will need to be developed and the limits of slurry concentration required to keep the rate of build up at practical levels will need to be established.

3.4. Two phase liquid solvents

In this process two liquid phases are formed once CO_2 is absorbed in the solvent. The lower phase will contain most of the absorbed CO_2.

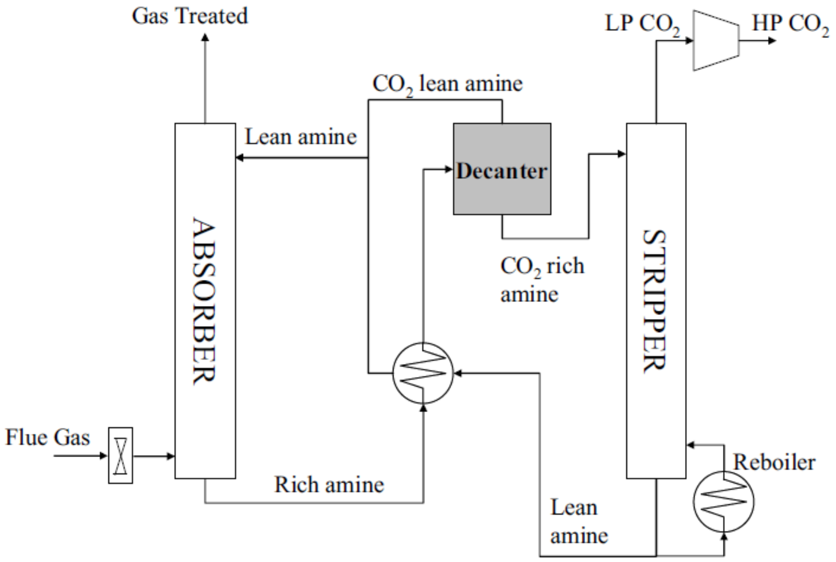


Figure 12 Simplified process flow diagram of the IFP Energies Nouvelles DMX^{TM} process [Raynal et al 2011]

This liquid phase is separated out and sent for CO_2 regeneration. This results in a lower quantity of CO_2 rich solvent to be regenerated and thus reduces the regeneration energy requirement. The solvent used for this process has hydrophobic functionality under certain conditions. From the process engineering point of view the two-phase liquid/liquid separation is easier in design and operation than solid/liquid separation (precipitating solvents).

3.4.1. Energy requirement / Cost evaluation

Based on current research the reboiler duty can be reduced to 2.3 GJ/tonne and possibly as low as 2.1 GJ/tonne CO_2. As well, captured CO_2 is regenerated at higher pressure which will result in a reduced CO_2 compression energy requirement. The techno-economic process evaluation of the DMX-1™ process finally results in a CO_2 cost of about 56 €/tonne CO_2 which represents a significant reduction when comparing to the reference case estimated at about 75 €/tonne CO_2 with the same boundary conditions [Raynal et al 2011]. This reduction in capture cost is about 26%. Comparing with the NETL benchmark on the basis of this lower energy requirement a reduction of 35% of the thermal load could be made. The LCOE would reduce by about 35*0.47 = roughly 16%. The capital costs are expected to be similar with some extra costs for the decanting equipment offset by smaller sizes for columns and pumps. Some further small reduction due to reduced compression power could also be expected if the regeneration process proves suitable for operation at higher pressure.

3.4.2. *Thermodynamic and chemical equilibrium considerations*

These are similar to those for precipitating solvents and it is already interesting to note that the chosen solvent for the DMX process has a significantly lower heat of reaction at 60kJ/mol than the ~80kJ/mol for MEA. Apart from the effect of lower free energy of reaction on attainable solvent loading there is also an effect on the required absorption and regeneration temperature. These become lower and with wider spread as the heat of reaction falls. This implies that some refrigeration may be necessary as is the case with the chilled ammonia process.

3.4.3. *Current Status, technology readiness level and development requirements.*

University of Dortmund, Germany has been investigating a two-phase system ‘Thermomorphic Biphasic solvent’ for several years. The IFP concept ‘DMX’ solvent is under development by testing at a pilot plant in recent years and there are ongoing activities to perform pilot plant tests under real process conditions for biphasic solvents e.g. Octavius project (EU FP7) and the IFP DMX-1 process is under evaluation to be tested at Enel’s Brindisi pilot plant, Italy. The two phase de-mixing concept developed by NTNU will be tested at lab-pilot scale as part of the iCap project (EU FP7).

Although several groups are conducting or planning pilot testing there is a need for a firm validation of the process. The basic concept does however appear to be proven. The current assessment is that this technology is at TRL-4. If plans to test at pilot scale come to fruition this will raise to TRL-5 or possibly TRL-6 once successful long term runs have been completed.

This process needs to be evaluated under real process conditions. Further work on optimizing solvent formulation and composition based on operability, degradation and emissions as well as overall energy performance needs to be undertaken. This needs to include careful evaluation of any refrigeration energy requirements but also opportunities to use lower grade waste heat for regeneration. Two phase solvents have not been evaluated in detail for their environmental impact, so this area also needs to be looked into further. As the process relies on separation of liquids further work needs to be undertaken to establish the separation performance and the selection of liquid/liquid separation equipment.

3.5. Ionic Liquids

Ionic liquids are found to be suitable for CO_2 absorption due to their high physical and chemical CO_2 solubility. Moreover ionic liquids have high stability and negligible vapour pressure.

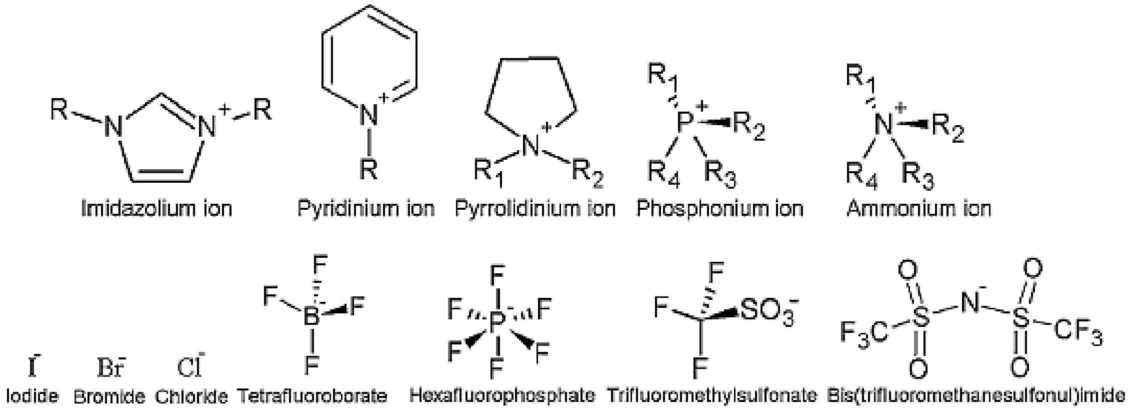


Figure 13 Some cations and anions constituting ionic liquids (ILs) [Hasib-ur-Rahmana et al. 2010]

These ionic liquids are inorganic or organic salts and are liquid with melting points below 100°C. These solvents are considered to be safer alternatives compared to volatile organic solvents for CO_2 absorption, due to their non-volatile nature at ambient conditions. Ionic liquids have been developed in order to modify the anion and cation to customize the solvent properties also known as designer solvents. Other ionic liquids such as poly-ionic liquids and reversible ionic liquids have also been developed. As well, research has been performed on the supported ionic liquid membranes e.g. supported ionic liquid on porous alumina membrane. This will give the advantages of low volatility and selectivity due to limited ionic liquid viscosity. Ionic liquids are also non-flammable at ambient and higher temperatures. Ionic liquids show potential for CO_2 absorption when the main challenges such as high viscosity, stability and regeneration can be overcome.

3.5.1. Energy requirement / Cost evaluation

It is suggested that ionic liquids can reduce the energy demand for CO_2 capture by as much as 16% when compared to the energy requirement of 30wt% MEA solvent. This is mainly due to relatively low regeneration energy requirements. Considering economics, the price of the solvent is the major issue. Since ionic liquids are only produced in small amounts for laboratory testing, the actual price is high but will decrease if a task specific ionic liquid is produced in industrial quantities.

3.5.2. Current Status, technology readiness level and development requirements.

Several research groups such as University of Notre Dame (USA), Imperial College (UK) and Chinese Universities, have been focusing mainly on improving ionic liquids. Georgia Tech Research Corporation has been developing reversible ionic liquids and DuPont is looking into the CO_2 solubility and phase behaviour for different ionic liquids. ION Engineering has developed proprietary ionic liquid for CO_2 capture with partners and contractors such as The University of Alabama, Worley Parsons, Energy and Environmental

Research Centre (EERC), EPRI (USA), Xcel Energy, Evonik and Eltron R&D [Shiflett et al 2011 and 2012]. A pilot plant unit at ION Engineering is in use and a 0.2 MW test at the EERC in North Dakota started in 2012.

Development of a commercially viable capture process based on ionic liquids is at a very early stage. It is still unclear whether the inherent limitations imposed by the rather high viscosity of such solvents can be overcome. Thus although the principle is well understood and basic parameters have been measured it is still not possible to formulate a viable application. Thus although scientifically very interesting, from a commercial perspective the technology readiness level is assessed as TRL-1

One of the important areas of improvement required is the viscosity of ionic liquids (66cP to 1110cP at 293K to 298K) this creates one of the main challenges when absorbing CO_2 thus increasing the energy required for solvent pumping and the potential for mass transfer problems and operational difficulties in engineered processes. Optimizing physical and chemical properties of ionic liquids should be researched further and improvements are required in lowering the thermal energy requirements for regeneration of CO_2 and solvent stability. More work is required in evaluating the toxicity of long chain ionic liquids and effects of cation/anions, this is because in some studies it is indicated that these solvents cannot be labelled ‘green solvents’ due to many of unknowns.

3.5.3. Thermodynamic and chemical equilibrium considerations

Ionic liquids can be made more absorptive to CO_2 by including suitable chemical reactive groups in the cation species. The properties can be changed from those of a physical absorbent obeying Henry’s law towards those of a chemical solvent. However the molecular weight of ionic liquids is quite high so that the absorptive capacity of chemically reactive formulations is inevitably significantly less than for MEA or other amines. The chart illustrates the equilibrium concentrations for MEA as compared to three candidate ionic liquids. Thus from the chemical/physical equilibrium standpoint these solvents are more likely to be useful in high partial pressure applications such as exist in pre-combustion capture. Because ionic liquids have very low vapour pressure and can be more thermally stable than amines it may be possible to regenerate at higher temperatures and hence pressures thus saving on CO_2 compression energy.

The viscosity of ionic liquids is inherently high and this is a potential barrier to rapid mass transfer in contacting devices. Alternatives to conventional packed columns which offer higher shear are likely to be needed, for example spray towers or high-G contactors might be considered.

There are a very large number of possible ionic liquids with cationic species running into hundreds and around 20 common anionic species. The anionic species are grouped according to their basic chemical structure and properties can be fine tuned by varying for example the length of alkyl groups. Correlations have been developed to aid prediction of properties and can be useful in guiding the search for combinations most suited to CO_2 capture.

In summary ionic liquids may struggle to compete with conventional absorption systems because their absorption capacity is likely to be much lower.

Their unique properties may be more suited to membrane separation applications. The key reasons for this are a) that the cation can be tailored to have a very high solubility for CO_2 so that a membrane formed of the ionic liquid has a very high selectivity and b) it is possible to make very thin films on a suitable support. Furthermore a support of a second membrane with very high permeability low selectivity can yield a composite membrane with both high selectivity and permeance.

3.6. Membrane separation

3.6.1. General issues

It is worth at this stage discussing the key properties of membranes and their potential for CO_2 separation as the next sections cover various developments in membranes for post combustion separation of CO_2. As discussed earlier there is a theoretical minimum work for separation of CO_2 from flue gases. This work is equivalent to that which would have to be expended if the CO_2 was separated from the flue gas through a perfectly selective and infinitely permeable membrane using isothermal compression to draw the CO_2 through and compress it to atmospheric pressure. This sets a theoretical benchmark for the minimum work per tonne for a thermodynamically reversible separation. Because the separation process is part of a larger system i.e. the fuel combustion and power generation process, researchers have identified a combination which further reduces the theoretical minimum work. This can be done by allowing the combustion air necessary for the process to act as sweep gas for a second stage membrane with the final flue gas stream on the retentate side. The effect is to recycle CO_2 to the boiler thus raising the partial pressure of CO_2 in the flue gas which has the effect of reducing the minimum work of separation. Note that there is no work of separation in the second stage membrane if this is infinitely permeable and selective as there is no need for compression. The reason that this approach can reduce the energy penalty is that the recycle of CO_2 dilutes the air and lowers flame temperatures. However as the power generation process does not utilise the full flame temperature in its working cycle the additional work is made available without any additional energy penalty. Fig 14 shows the overall arrangement of the two membrane stages needed to achieve this.

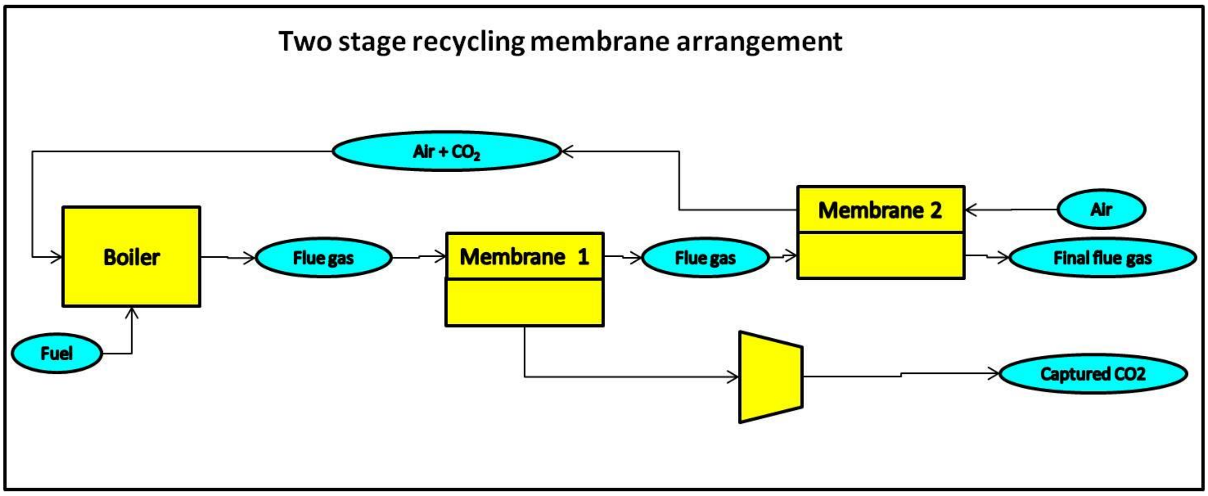


Figure 14 Two stage recycling membrane arrangement

Figure 15 illustrates how the concentrations of CO_2 and oxygen in the flue gases will change as the fraction of CO_2 crossing the second membrane as recycle increases. It also shows how the effect on total flow of air and CO_2 to the boiler.

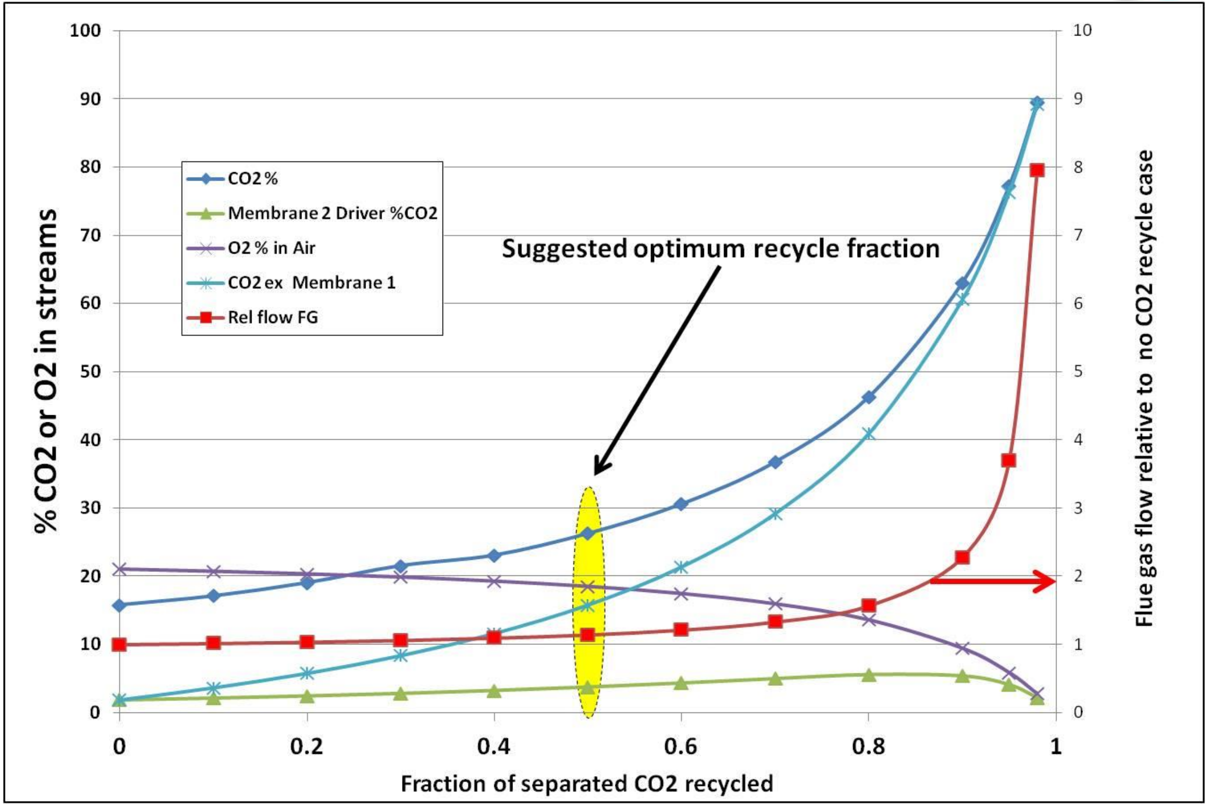


Figure 15 Optimisation of recycle fraction in two stage membrane process

The diagram shows the extent to which this arrangement can be exploited. An absolute limitation is the reducing oxygen content (purple line) which at around 12% would no longer support combustion. Practically, for a stable flame, a content of at least 17-18% is required. A second limitation is the increasing air and flue gas flow (red line right axis) which will absorb increasing amounts of power in the boiler fans. Respecting these limits, recycle ratios could be increased to around 0.5 which raises the CO_2 content at the outlet of the first membrane from 1.83 % to 15.7% in the example. This greatly lowers the amount of vacuum required in the lowest pressure permeate compressor and also reduces the number of compression stages needed. 50% is the value chosen for the MTR membrane process discussed later in this report. The calculated theoretical work of separation drops from 0.15 GJ/tonne CO_2 to 0.075 GJ/tonne, which is roughly half. Thus the practical compression requirement should drop by a similar amount. However this is an ideal calculation, which does not take into account the energy required to overcome resistance to flow through and across the membrane or increased fan power because of the larger flue-gas flow which is roughly 14% higher as a result of the recirculation. The extra power consumed by the fans solely as a result of these pressure drops is considerable as illustrated by the example of the MTR membrane estimated in detail by NETL. In their evaluation the extra power directly required by the membranes consists of about 45% for the fans and 55% for the permeate vacuum compressor. Nevertheless this process arrangement has considerable potential to reduce both membrane area and compression power in membrane separation systems.

Another factor affecting the permeate compression conditions is the selectivity between CO_2 and water vapour. There is a considerable concentration of water vapour in typical flue gas and if water vapour co-permeates it will act as a sweep gas substantially lowering the partial pressure of CO_2 in the permeate. However any beneficial effects on overall power are largely counterbalanced by the need to compress a far larger permeate flow, until a pressure is reached at which the water vapour can be condensed out.

The other practical limitation is the increasing size and hence cost of the second membrane as the recycle increases.

3.6.2. Cost and performance of membrane separation systems

There are a number of different types of material from which membranes can be fabricated. Within each type variations in structure and manufacture can endow a range of permeabilities and selectivities. However, as a general rule, selectivity increases result in permeability decreases and when plotted on a log/log scale there is straight line termed the “Upper bound” which delineates the limits of performance for each class of membrane. This relationship, first proposed by Robeson in 1991, limits to some extent the scope for improvements but also helps direct research. The “upper bound” has been reviewed recently to take account of performance advances but only minor shifts resulted. The other key variable in membrane performance is the thickness since the rate of permeance to gas is proportional to the inverse of the thickness. The achievable minimum thickness will depend on the ability to avoid defects in the manufacturing process and, where necessary, to provide the structural support needed to prevent damage to the membrane due to the prevailing differential pressure during operation. The costs of membranes are generally taken as per unit area with typical prices of around \$50/m^2. The cost of membrane elements is not expected to show much economy of scale other than quantity discounts. An allowance for structure and piping has to be made and, unlike the membrane elements, the costs for these will benefit from some economies of scale.

A major cost of membrane systems is compression or vacuum pumping equipment. The extra power consumed by the compression will also reflect in increased capital cost of the main generating plant and play through into the LCOE in much the same way as for post combustion solvent systems. Thus arrangements, which can minimise compression power are likely to have lower increases in LCOE. It is noted that estimates tend to assign much higher costs per kW to vacuum pumps than to compressors. For very large machines where centrifugal or axial compression is appropriate there should in principal be little difference in cost per kW for a given power. However where vacuum pumping is based on a different type of machine, for example a liquid ring pump, unit costs will be higher. It is thus important in assessing estimates to analyse what type of compression machinery is specified and what type is actually needed.

3.7. Polymeric and Hybrid membranes

Polymeric membranes have been used at low temperature to separate CO_2 at industrial scale for several years e.g. in natural gas CO_2 separation. There are two types of general polymeric membranes available for CO_2 separation, glassy and rubbery membranes.

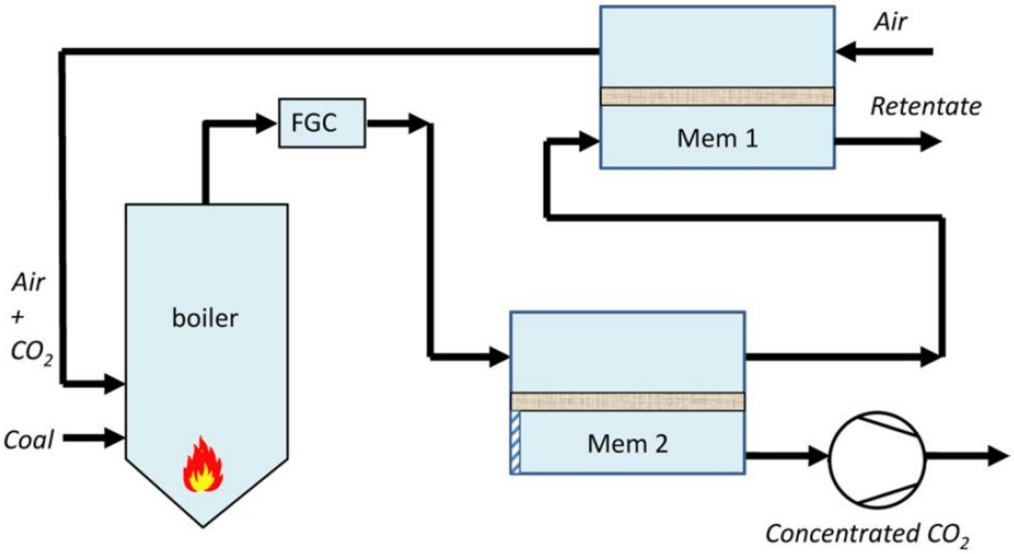


Figure 16 Schematic illustration of the membrane concept for CO_2 separation from coal-fired power plant. (FGC: flue gas cleaning, Mem: membrane module) [Franz et al. 2013]

Glassy membranes are rigid, with lower permeability and operate below the glass transition temperature, while rubbery membranes are flexible with higher permeability and operate at above the glass transition temperature. These dense phase polymer membranes show CO_2/N_2 selectivity in the range of 40/70 and permeability 570-120 Barrer. A CO_2 purity of up to 90% or more is obtained when selectivity of CO_2/N_2 is 70/80 Barrer with a CO_2 capture rate of 80% from flue gas with 15% CO_2. Therefore a multi-stage membrane is required to achieve acceptable captured CO_2 purity (see Figure 16). Another type of membrane is fixed site membrane where a chemical reaction takes place in the presence of water on both sides of the membrane. The presence of water limits the permeability; the selectivity of these membranes for CO_2/N_2 is 50-230 with CO_2 permeance in the range of 1000-1 GPU. Still it is difficult to achieve captured CO_2 purity of 90% or more with 80% CO_2 capture rate with 15% CO_2 in the flue gas.

Hybrid membranes made from polymeric membranes and integrated nano-particles show the potential in increased CO_2 flux and selectivity when compared to polymeric membranes. These membranes show selectivity of above 100 and flux of more than $0.7 Sm^3/m^2.h.bar$. Another type of membrane is liquid membrane which also shows the potential of higher CO_2 selectivity of up to 45000. A single stage membrane process is feasible for these membranes.

The main advantage of polymeric membrane based CO_2 separation is that it produces a non-hazardous waste stream and thus has minimal environmental impact. Membranes can be designed in modules which allows for scale up of the unit and retrofit. There have been several studies in which the suitability of membrane separation is investigated for coal and NGCC power plants.

3.7.1. Energy requirement / Cost evaluation

Cost evaluation for coal fired power plant was reported by Ramasubramanian et al. 2012. At a low membrane price of \$2.5/f^{t2} (\$27/m^2), the purely membrane-based air-sweep process can result in a cost of electricity (LCOE) increase of 33-35% and a capture cost of \$24/t CO_2 at a CO_2 permeance of 3000GPU, a CO_2/N_2 selectivity of about 140 and a feed pressure of close to 1bar.

Analysis of the cost and material balances for the MTR membrane process [NETL 2012] reveals a 20% increase in fuel consumption due to the additional parasitic loads, much less than that for the baseline Econamine FG Plus process (38%). This increase in fuel to supply the increased electrical load can be divided into three elements. Approximately 47% is for CO_2 compression, 29% is for the vacuum compression and 24% for the increased pressure drop in the flue gas system and other utilities. Specific energy calculates as 0.45GJ/tonne captured and 0.55GJ/tonne abated. The LCOE cost increase calculated by NETL is only 70% of that for the baseline Econamine FG Plus process i.e. a 30% reduction is projected. This does however rely on assumptions about the cost and performance of the membrane modules. In this study costs were evaluated based on a future membrane cost of 80\$/m^2 which compares with 140\$/m^2 near term target. Installed cost of the CO_2 separation plant was however about \$154/m^2. Permeance was a somewhat optimistic 3500 GPU but selectivity CO_2/N_2 was taken as a reasonably conservative 35. Even with these comparatively high costs per m^2 when compared with other projections the cost of the separation equipment i.e. the membranes plus vacuum pump was less than for the comparable benchmark Econamine FG Plus process. The costs for the vacuum pump were not reported separately but based on the calculated power and taking unit cost as 2X that of the main CO_2 compressor, it is estimated to represent about 25% of the separation equipment, meaning that the membranes were costed at around \$113/m^2 installed.

Whilst much more detailed analysis of costs is warranted and recognising the wide range of per m^2 costs reported in the literature the technology nevertheless appears to promise considerable reductions in cost of capture.

3.7.2. Current Status, technology readiness level and development requirements.

Currently there are several research organizations and companies developing improved membranes and carrying out pilot plant testing. The EU project nanoGLOWA has tested a diffusion transport membrane and a fixed site carrier membrane at a power plant in Germany. The NTNU patented polyvinylamine (PVAm) membrane together with fixed amine groups (which acts as carrier for CO_2) i.e. fixed site membrane (FCS), is evaluated at a pilot plant at an EDP power plant in Portugal. The PVAm+FCS membrane test resulted in a promising result of extremely high separation of CO_2 at a low feed pressure (maximum 2 bar) condition.

Membrane Technology Research Inc (MTR) is testing their membrane Polaris in a 1MW unit at DOE’s National Carbon Capture Center (NCC) in Wilsonville, Alabama from 2013. The flue gas is taken from Alabama Power’s Gaston Power plant Unit5 (supercritical pulverized coal unit). Other organizations such as MEMFO, NTNU, and SINTEF Norway; Membrane Technology Group an Twente University, The Netherlands; Centre of Membrane Technology and NJIT, USA; and RTI International, USA are active in the area of membrane based CO_2 separation process development.

There are several tests of membranes in this application at reasonable scale and membranes have been used at larger scale for the similar separation of CO_2 from natural gas. The technology readiness level is assessed as TRL-6. It is further noted that given the widespread deployment of membranes in other applications development could proceed relatively quickly.

Further material development and tests of the impact of impurities on the membrane need to be performed. Pilot plant tests at larger scale to the level of 10MWe are also required.

3.8. Polymeric membrane and low temperature separation

This process utilises a membrane stage to concentrate CO_2 in the permeate stream and then undertakes liquefaction of the CO_2 to achieve the necessary purity. This minimises the energy requirements of the liquefaction process as the majority of the N_2 has been excluded by the membrane stage. The second and third membrane stages are to ensure high CO_2 recovery. The second membrane stage recovers CO_2 from the retentate of the first membrane stage and recycles this back to the process feed through the coal burner. The third membrane stage recovers CO_2 from the liquefaction column off-gas stream and recycles the permeate stream back to the first membrane stage permeate, while the retentate stream is recycled back to the first membrane stage feed stream. Critically, a sweep gas is applied to the second membrane stage to generate the pressure driving force. This maximises CO_2 recovery while minimising the membrane area, as well as avoiding the high energy duty of a compressor or vacuum pump. It is this sweep gas, the combustion air for the coal burner, which Merkel et al. 2010, indicates makes the membrane design cost competitive. This is because the recycle of CO_2 from the second membrane stage through the coal burner increases the CO_2 partial pressure in the flue gas going to the first membrane stage, and hence improves separation performance.

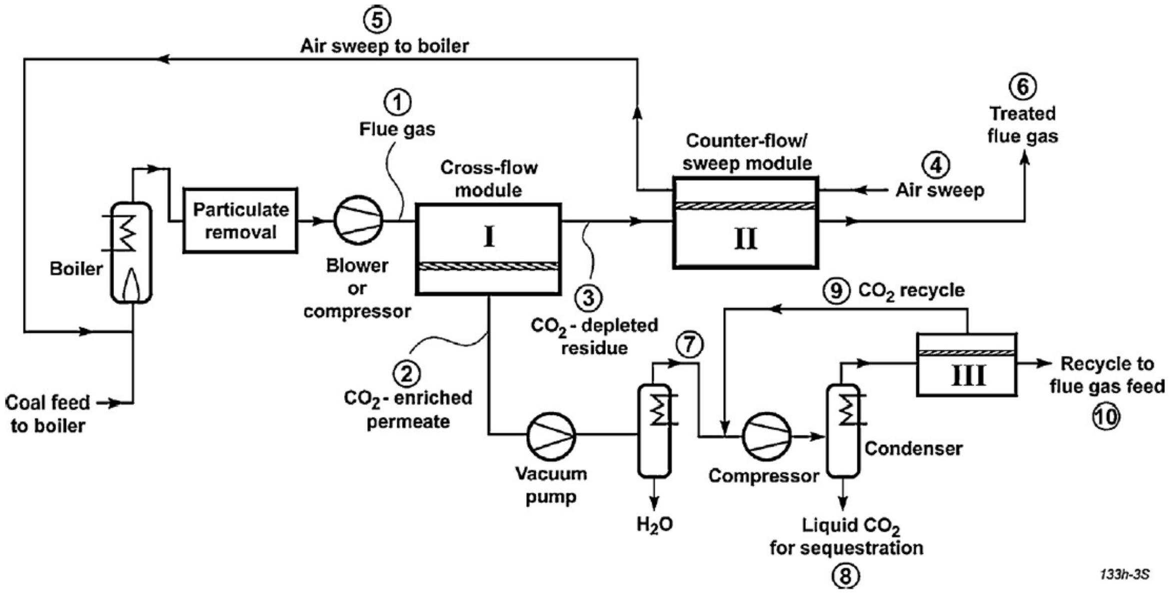


Figure 17 A post-combustion carbon capture plant scenario with three CO_2 selective membrane stages [Merkel et al. 2010]

Another configuration for this process involves operating the membrane at low temperature (-25°C to -45°C). The membrane CO_2/N_2 selectivity and permeance increases significantly when operated at these temperatures. However this concept is more complicated and requires significant heat and work integration.

First evaluation of this technology shows that the process has better performance when compared to an MEA based process when the CO_2 concentration in flue gas is in the range of

15-30%. A lab scale test at 0.1 MWe for this technology by Hasse et al 2012 showed that this technology has potential for performance improvements.

3.8.1. Energy requirement / Cost evaluation

In the study performed by Scholes et al 2013, the cost of CO_2 capture is estimated of 42 US$ per tonne of CO_2 avoided for a 2 stages membrane gas separation process, when compared to an MEA based process of 55 US$ per tonne of CO_2 avoided. SINTEF has also studied the costs and energy requirements of hybrid cryogenic systems and evaluated those situations where it is most likely to be applicable [Jordal et al 2012]. Marginal improvements were deemed possible in post combustion capture and more substantial gains in pre-combustion systems.

This hybrid process has the potential to improve on the performance of a membrane only process. It may allow the use of less selective membranes which are likely to be cheaper. Liquefaction and pumping of recovered CO_2 will also reduce the costs and energy consumption for CO_2 compression although this gain will be offset by additional compression costs in the process. A detailed evaluation of this trade off needs to be performed.

3.8.2. Current Status, technology readiness level and development requirements.

Currently Air Liquide has run a bench-scale test operation for the membrane in operation at -25°C to -45°C. Linde Engineering, Germany is also involved in developing low temperature CO_2 purification technology.

The majority of this process is at a similar development stage to that of the full membrane process but membrane performance requirements will be more relaxed. The CO_2 liquefaction element can be based on well developed cryogenic gas processing technology. The technology readiness level is therefore also assessed as TRL-6

This hybrid technology needs to be tested next at the scale of 1MW-10MW.

3.9. Other hybrid membrane systems

The key to the dual membrane system is the use of combustion air as a sweep gas in the second stage of the system. In fact air (or oxygen in oxycombustion systems) could potentially be used as a sweep gas for other separation systems such as solvent stripping of solid sorbent regeneration. Also the first stage of the separation process where the CO_2 partial pressure has been raised by the recycling could be conducted using absorption, cryogenics or adsorption. Thus a large number of hybrid variants are potentially worth investigation. There is some evidence that researchers are starting to look at these alternatives for example [Freeman 2014] has examined a system where the first stage separation of the MTR system is replaced by a conventional solvent absorption system.

3.10. Gelled Ionic Liquid-Based Membranes

Gel-RTILs (Room Temperature Ionic Liquids) are formed by incorporating low molecular weight organic gelators (LMOGs) into RTILs – H-bonding, van der Waals interactions, and pi-pi stacking between LMOG and RTIL are responsible for physical gelation. Gel-RTIL maintains CO_2 affinity and permeability characteristics of RTILs. A low fraction of LMOG is required, typically 1-5 wt%. Free RTIL provides for fast liquid-like diffusion and enhanced flux. This also provides an increase in mechanical and thermal properties of RTIL upon gelation. Gelation is a thermo-reversible process with transition temperatures ranging from 20 to 180°C. This membrane has demonstrated high perm-selectivity for CO_2 over other components of coal-fired power plant exhaust gas.

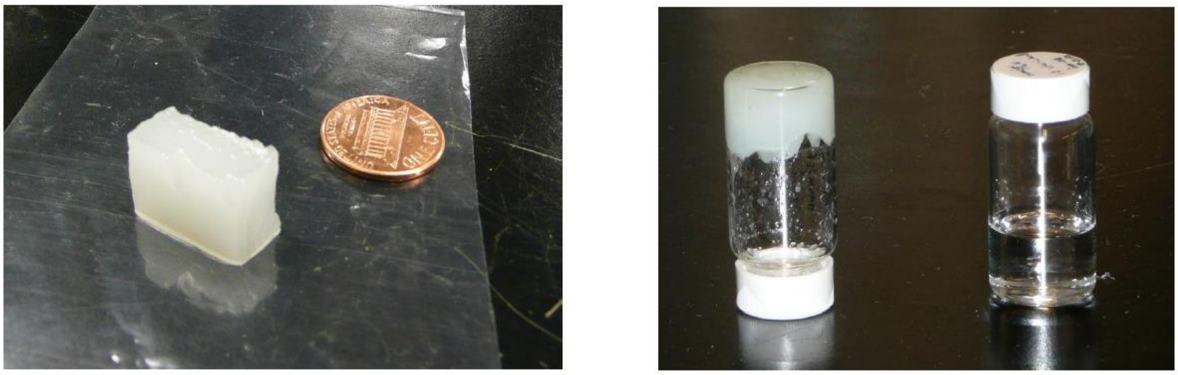

Gelled hmim/Tf_2N gelled neat

Figure 18 RTILs Gelled membrane (hmim/Tf2N 98.5 wt% with 12-hydroxy stearic acid 1.5 wt%) [Noble et al 2013]

3.10.1. Current Status, technology readiness level and development requirements.

Under DOE's funded project, University of Colorado (CU), Boulder is working on selective layer material design and synthesis for these membranes. Fabrication of these gel-RTIL and RTIL/Poly(RTIL) composite membranes by Ultrasonic-atomized spray-coating is done by Los Alamos National Laboratory (LANL) and 3M (USA). Based on the tests and results for these membranes Electric Power Research Institute (EPRI) will perform process evaluation.

The use of ionic liquids as CO_2 solvents while scientifically interesting has yet to be shown to offer a real advantage in a commercial system. A convincing application of this type has yet to be formulated thus the technology readiness level is assessed as TRL-1. The application in membranes appears to offer a more viable application with some possibilities of attaining a breakthrough in performance. However the research is still at the stage of finding methods of fabrication of the membranes so that they exhibit the necessary high permeance and stability. The performance can then be validated under laboratory conditions. Thus the technology readiness level is assessed as being at TRL-2.

It is required to develop a quantitative understanding of how the deposited material is distributed in the composite membrane both within the support and through the selective layer thickness. Multiple Layer coatings and post-processing can be used to increase the permeability and selectivity of the final membrane. Complete parametric studies are required to further understand the influences of membrane performance characteristics on process economics.

In order to enhance the potential for industrial interest, evaluation of these membranes for CO_2/CH_4 separation (natural gas treatment) will be evaluated. The selectivity target is CO_2/CH_4 selectivities >20 at low pressure and ambient temperature.

3.11. Pressurized post combustion capture

Sargas of Norway has proposed to use a coal fired pressurised fluidised bed boiler in post combustion applications to take advantage of much higher partial pressures of CO_2. (Bringelsson 2009). Energy would be expended in compressing air into the boiler. However energy would be recovered by re-expanding the flue gas after CO_2 capture with greater efficiencies achieved the hotter the starting temperature of this expansion. In effect a Brayton cycle is added across the main Rankine cycle of the steam boiler.

They have also proposed a similar process for gas turbine based power plant whereby the capture of CO_2 would occur at high pressure prior to expansion. The proposal is to use hot potassium carbonate as the absorption medium. The hot flue gas has first to be cooled to about 100C before entering the capture plant but is reheated using heat exchange so that most of the heat is recovered. The pressurised gas, scrubbed of CO_2, is then expanded to generate power. Sargas formed an alliance with GE in 2012 to develop the technology based initially on the LMS100 gas turbine. However there are few published technical details after 2009.

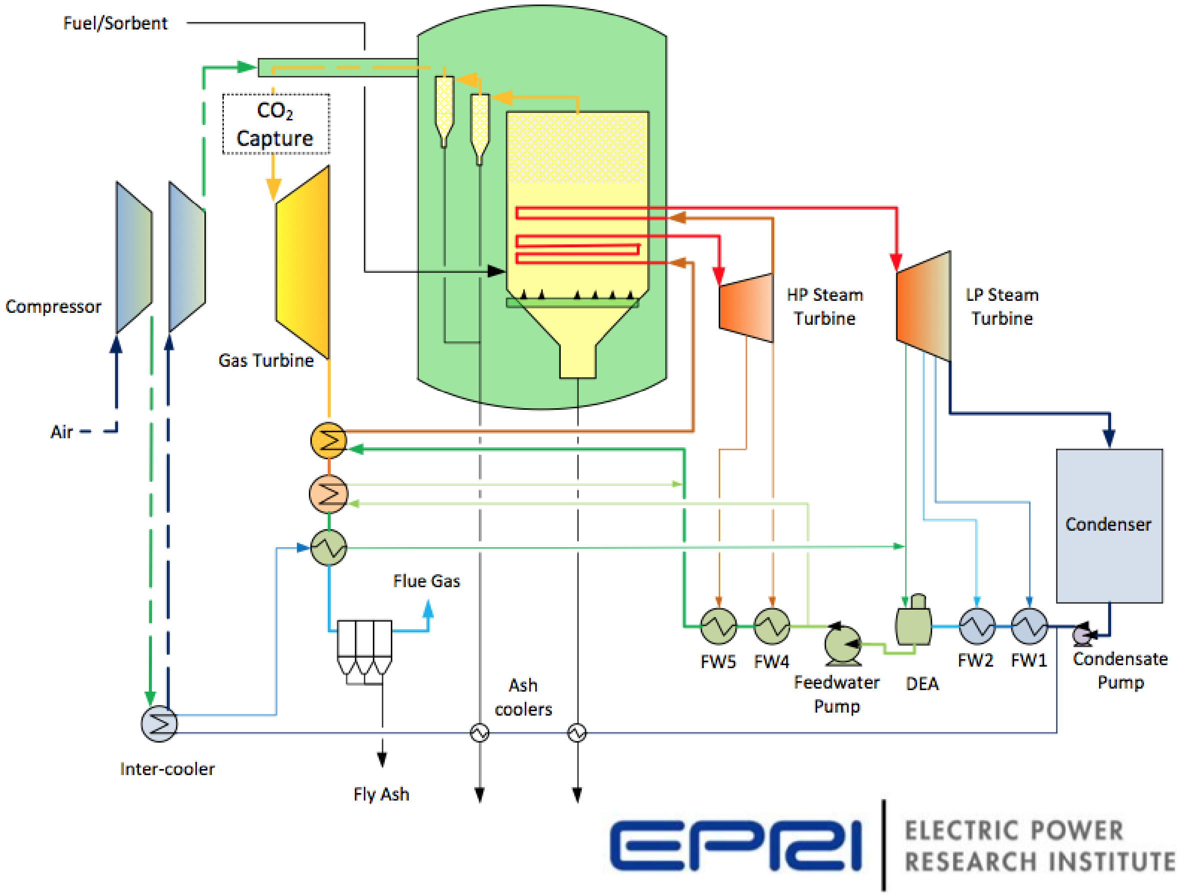


Figure 19 Pressurised post combustion capture as proposed by Sargas.

3.11.1. Current Status, technology readiness level and development requirements.

Apart from the alliance with GE development of the proposed technology appears to be dormant since pilot plant tests results were reported in 2009. Tests were performed on the hot Potassium absorption system at a pressure of approximately 10bar. The operation of the main subsystems required is thus validated and the technology readiness level is assessed as TRL-5. Bubbling bed pressurised fluidised bed combustion (PFBC) has been demonstrated at a large scale, for example a 360MWe plant at Karita in Japan and is at TRL-8, but further work is needed to demonstrate it as a commercially competitive technology to conventional pulverised coal combustion. Also further work needs to be done to establish the overall energy efficiency of the systems with CO_2 capture.

3.12. Enzyme catalysed CO_2 absorption/desorption

Enzymes can be used to catalyse the CO_2 absorption process in carbonate/bicarbonate (potassium carbonate) solvents. This is based on natural catalysis of CO_2/O_2 in the respiration system catalysed by the enzyme Carbonic Anhydrase II (CA II). These pure aqueous carbonate/bicarbonate solvents exhibit severe limitations in the CO_2 absorption rate. Thus there are several formulations available of carbonate/bicarbonate solvent together with amine based solvent which overcome this limitation in CO_2 absorption rate. Similarly tertiary amine based solvent such as Methyldiethanolamine (MDEA) also suffers from low CO_2 absorption rate and require an activator to enhance the CO_2 absorption rate.

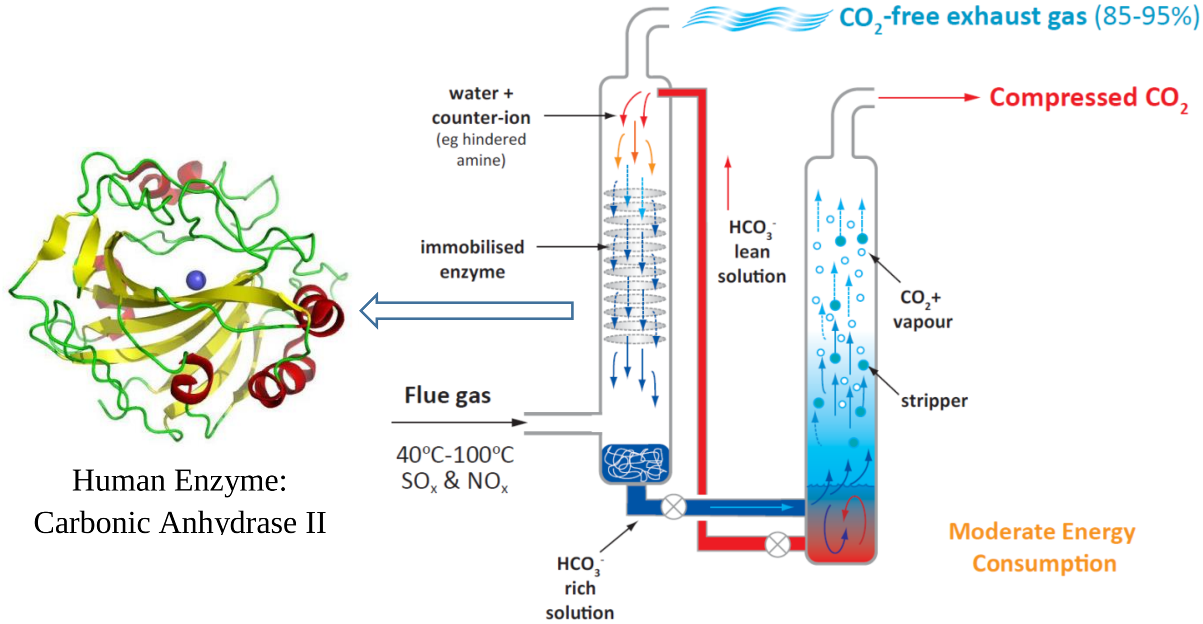


Figure 20 Concept for the use of enzymes to capture carbon dioxide employing the conventional absorber/stripper configuration [CSIRO 2012]

Enzymes have potential to be used as an activator to accelerate the CO_2 absorption rate. In this process the enzymes are clustered together in a cross-linked enzyme aggregate (CLEA) and filtration is used to separate the enzyme from the CO_2 rich solvent before solvent is send for CO_2 regeneration. From the environmental perspective, the inorganic carbonate/bicarbonate solvent activated with enzyme is very favourable as no emission will occur. One of the main challenges related to enzymes is the stability of enzymes in the chemical and physical environment especially at higher temperature. Industrial enzymes are routinely immobilised, i.e. non-destructively bound to inert supports such as silica, resins, nylon and polyurethane for use in reactors. Immobilisation often increases stability of enzymes to pH and temperature, and extends their useful life as well as improving their ease of handling, separation and recovery [Mateo et al. 2007]. Figure 20 shows the conceptual process diagram of immobilised enzyme in the absorber wetted by an aqueous solution containing counter-ions.

3.12.1. Energy requirement / Cost evaluation

CO_2 Solutions, Canada enzymatic technology showed an energy cost reduction of at least 33% compared to existing carbon capture technologies when employed to capture 90% of the CO_2 emissions from natural gas combustion at a typical in-situ oil sands operation. Codexis has claimed that their enzyme based process could significantly reduce CAPEX (capital cost), with a ~95% reduction in CO_2 absorber column size with low-energy solvent MDEA and ~80% reduction in desorber volume without use of structured packings.

3.12.2. Cost considerations

The main reduction in costs would appear to be for the capital cost of the absorption column. In the baseline estimate about 67% of the capex increase is due to the capture system of which 10% is for compression. This leaves 60% of the capex increase as a target for cost reduction through having a smaller absorption column and other capture process equipment. Fabricating and erecting the column will be a major part of this and reducing its size will affect that element of the overall cost. The basis for the 95% size reduction of the absorber is not clear. Only a detailed cost estimate could reveal the full potential. Considerations are that the reaction rate of CO_2 with the solvent is not the only limitation to column sizing. There will be a limit to the gas velocity in a conventional packed absorber tower which will limit the minimum cross sectional area and also sufficient theoretical stages have to be provided to achieve the desired capture efficiency which will limit the minimum absorber height. Each 10% reduction in capital cost would translate into a reduction in the extra cost of electricity of about 7% using simple factoring. More evidence would need to be produced from process modelling and pilot plant results to validate claims of an energy consumption reduction. Nevertheless the capex for capture plant is a significant driver of the increase in LCOE but claims for such large reductions below the cost of conventional post combustion capture should be carefully scrutinised.

3.12.3. Thermodynamic considerations

The action of the enzymes is similar to that of the chemical promoters used in solvent formulations. The key effect is thus to enhance mass transfer and thus reduce the size of the absorption plant. The equilibria of the absorption reactions are not changed although in principle a closer approach to equilibrium might be obtained. It is thus not entirely clear how the use of enzymes will reduce energy consumption as claimed.

3.12.4. Current Status, technology readiness level and development requirements.

Currently CO_2 Solutions (Canada), Novozymes and Carbozymes are developing their proprietary enzymes for CO_2 absorption processes. This technology is still at a proof of concept level.

As the work on developing suitable enzymes is only at proof of concept stage the technology readiness level is assessed as TRL-1.

It is important that the enzymes are evaluated under real flue gas conditions and that the effect of flue gas impurities such as SOx and NOx are looked into. Solvent reclaiming processes for enzyme activated solvents also need to be assessed. Long term pilot plant testing is required to develop further understanding of this concept and assess the cost benefit.

3.13. Algae based CO_2 capture

Biological carbon capture describes the process of using plants to capture, react and fix CO_2 through the photosynthesis reaction. While the photosynthesis reaction involves a complex set of light and dark chemical reactions, it can be described as reacting light energy, water and CO_2 to form oxygen and simple sugars, and expressed as the generic formula:

$$6CO_2 + 6H_2O + \text{light} \rightarrow C_6H_{12}O_6 + 6O_2$$

In this reaction, $C_6H_{12}O_6$ represents the sugars which are metabolized further by the plant into more complex sugars, starches, and lipids. In most plant species, photosynthesis is an inefficient reaction with slow kinetics. This is especially the case for larger plant species which have to expend significant amounts of energy to build their structure, grow foliage, uptake and transport water, and reproduce. With simpler and smaller plants, the efficiency of the photosynthesis reaction (light energy to chemical energy) is comparatively higher as they do not need to invest as much energy to build large structures. At the extreme end of this scale are single cell algae. They are the smallest and simplest forms of plants and they lack traditional plant structures relying instead on water as their supporting structure. By not having to invest energy in growing roots, leaves and flowers, algae can commit all of their energy into reproduction. The simplest way to promote the growth of algae is to supply them with abundant amounts of CO_2 and light. As the amount of sunlight that shines on any one location cannot be changed, the only improvement is to supply them with CO_2 and mix them so that each alga has some exposure to the water's surface to conduct its light reactions before being mixed under water where the light is dim.

A photo bioreactor is a device that can be used to give better condition for the microalgae to go with the photosynthesis process, it is designed to be able to adjust the condition of light, temperature, pH, CO_2 and nutrients. In this system, a pump is used to make the cultures re-circulated within the tube, and the CO_2 will be pumped into these tubes with the air pumps. This photo-bioreactor can be used for the outdoor mass cultures due to the large illumination surface.

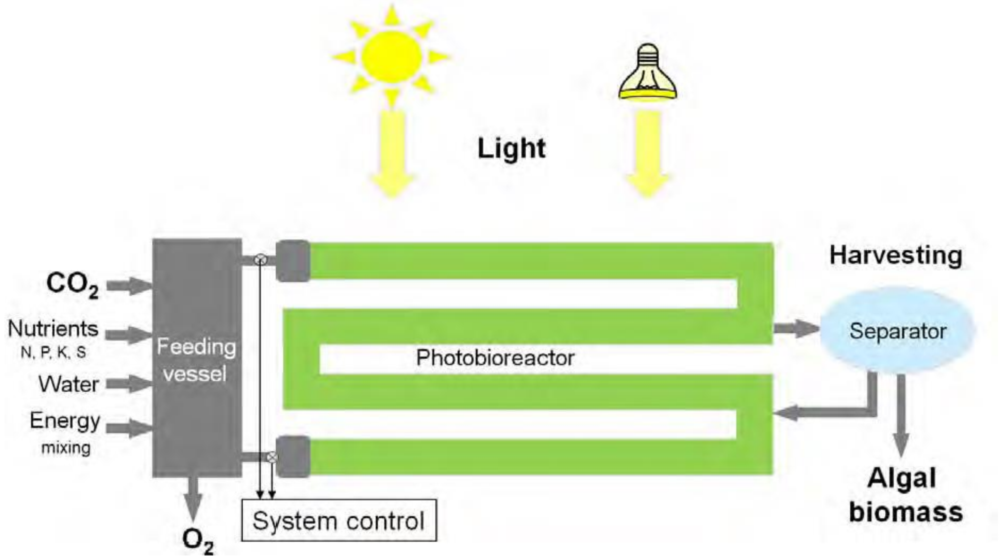


Figure 21 Design principle of a tubular photo bioreactor system [CO2-to-Bio 2012]

Most photo bioreactors differ in the design of the transparent vessel, which in this example would be closed loop glass tubes with a diameter between 3-5 cm. The light system can be based on either natural or artificial light – or a combination of the two.

3.13.1. Energy requirement / Cost evaluation

CO_2 capture by microalgae has high costs (energy for pumping the medium, compressing air, harvesting biomass, etc.), but this process has also benefits: (i) CO_2 conversion to biomass; and (ii) production of valuable products.

3.13.2. Thermodynamic considerations

Harvesting of solar energy can be accomplished by a range of technologies such as solar thermal, solar electric arrays and energy crop harvesting. The yields of energy crop harvesting are in general less than 1% of the incident solar energy whereas solar PV systems can reach much higher levels albeit reduced by shading effects. The 15gm/day/m^2 of CO_2 is roughly in line with that from other energy crops indicating that very large areas would have to be used to replace a commercial scale power plant.

3.13.3. Current Status, technology readiness level and development requirements.

Researchers at EniTecnologie in Italy conducted a field experiment of CO_2 uptake by algae in a raceway pond (which is a shallow artificial pond used in the cultivation of algae; it is divided into a rectangular grid, with each rectangle containing one channel in the shape of an oval). The Tetraselmis suecica algae were supplied with CO_2 from natural gas turbine flue gas. The experiment was conducted between the months of April to November and it measured the rates of production correlated to ambient temperature and available light.

EniTechnolgie reported growth rates as mass of dry algae produced each day per square meter of raceway. During the April to November time period, productivity ranged between 10 and 30 g/m^2/day. The CO_2 uptake represents roughly half the weight of the dry algae, or ~5 to 15 g CO_2/m^2/day. Green Fuel is investigating photo bioreactors which bubble flue gas through high-rate micro-algae for CO_2 and NOx removal. Idaho National Lab is investigating the uptake of inorganic carbon in a photosynthetic reactor with bacteria (Cyanobacterial: Synechococcus sp. strain PCC 8806) which raises the pH and promotes $CaCO_3$ precipitation. ORNL and Ohio State are validating bench-scale photo bioreactor designs to grow algae from flue gas.

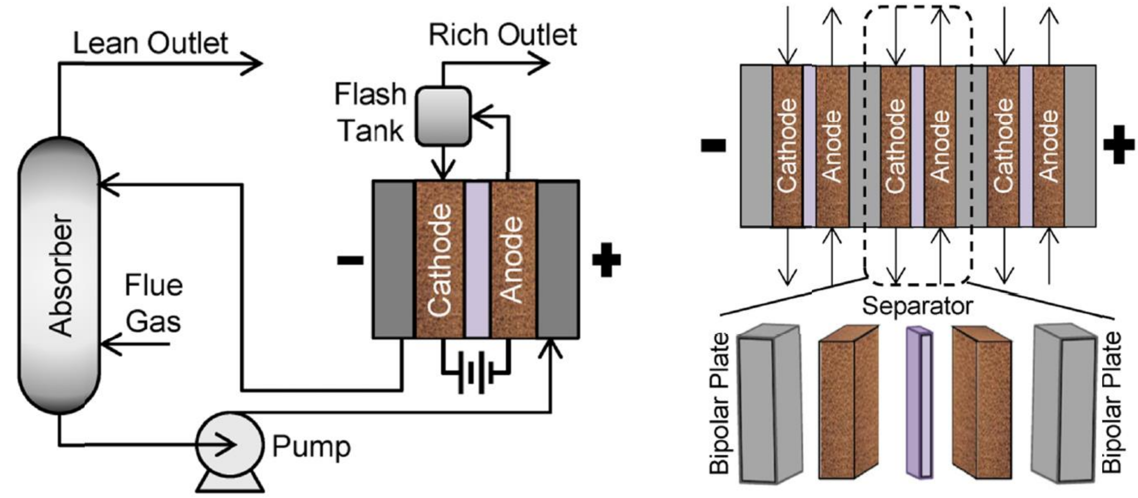
Duke Energy's project at East Bend Power Plant in Kentucky is to demonstrate an algae-based system for CO_2 mitigation from coal-fired power plants. Project participants include the University of Kentucky Center for Applied Energy Research and the University of Kentucky Department of Bio systems and Agriculture Engineering. Several other companies and organizations are testing this technology such a Latrobe University, Australia; KEPCO, South Korea, NALCO, India etc.

It is questionable whether work on micro-algae should be included in the scan of capture technologies. Production of high value chemicals may be a more fruitful application more suited to the practical scale and economics. To qualify for large scale capture the application needs to be formulated on the same scale as commercial fossil fuel power plant. It is also questioned whether at this scale suitably large sites could be found. The CO_2 emissions of a baseline coal fired power plant are just over 10,000 tonnes per day. To capture 90% of these emissions at the rate of 15gm/m^2/day would require an area of about 625 square km (a square 25km by 25km). This technology is thus assessed at TRL-1 for large power plants.

More work is needed to understand how regional weather effects will impact the productivity and marginal cost impacts. An economic assessment of processes in different embodiments (capture only, capture with co-firing, capture to biofuels) is needed to understand the cost of CO_2 capture. One of the main challenges in large scale production of microalgae to be used as a feedstock will be to increase the dry weight from ca 2% to 20% in order to get a sustainable production.

3.14. Electrochemically-mediated amine system

In order to reduce the energy penalty and eliminate solvent thermal regeneration a novel process of electrochemically-mediated amine regeneration (EMAR) is proposed by Stern et al. 2013. In this process the heat exchanger and stripper is replaced with an electrochemical cell. This concept offers the advantage of easier retrofitting as no integration is required with the plant steam cycle. Also probably lower CO_2 lean loading can be achieved. Therefore, this process has potential to improve the overall process economics by reducing absorber size and lowering system energy penalty.



(a) (b)

Figure 22 (a) Schematic diagram of EMAR process (b) A cross sectional view of EMAR electrochemical cell stack [Stern 2013]

The CO_2 reacts with an amine and it is subsequently decomposed in an electrochemical cell in a process similar to electrolysis. However the transfer of electrons is not directly to the CO_2 amine compound but between a metal and its cation. The cation once formed has greater affinity for the amine than the CO_2 which is this released. The metal ions of higher oxidation state are formed at the anode where they displace the CO_2 from the amine/CO_2 complex. The Metal ion amine complex which results is then reduced at the cathode to regenerate the amine which can then absorb more CO_2. The work of Stern concluded that only three transition metals might be suitable; Cr, Cu and Fe but that Cr and Fe would likely suffer oxidation from oxygen present in the flue gas. A system based on reduction of Cu^{++} to Cu was thus selected for further research. A number of different amines were also examined for applicability as a result of which EDA was found to be superior.

3.14.1. Energy requirement / Cost evaluation

The EMAR system claims several distinct advantages over traditional thermal scrubbing designs. The advantages claimed range from easing installation logistics, reduction in capital costs, to improved operational efficiency.

The half cell potential for the Cu^{++} to Cu reaction is 0.34 volts which is equivalent to a free energy of reaction of about 66kJ/mol. This is the reaction which occurs at the anode. The Cu^{++} displaces bound CO_2 releasing this at the anode. At the cathode the Cu^{++} amine complex is decomposed depositing copper and releasing lean amine for further reaction. The difference in these two potentials is the work required for the separation. In open circuit conditions this voltage was found to be of the order of 0.2 volts which equates to about 38kJ/mole with values falling as low as 0.12 volts at 80°C equivalent to 23kJ/mole. However it will be increased by losses in the electrochemical cell which include electrode over-potentials, ionic and conductive resistances and also a Faradaic efficiency loss whereby not all electrons flowing result in release of CO_2. Furthermore the work is supplied as DC electrical energy which is generated at the efficiency of the power plant less the conversion efficiency from AC to DC. A further interesting feature of the system is the ability to operate under high pressure. The CO_2 would then be released at pressure so that less compression energy is required. The increased partial pressure of CO_2 however raises the cell potential required but this direct use of electric energy for compression is more efficient than using mechanical compression. A practical limitation however is the solubility of CO_2 in the solvent which limits how much is released as gas so that using pressures above around 15bar is not efficient.

The experimental work so far has concluded that at practical flux rates an electrical consumption of 100kJ/mole would be required, far higher than that for estimates based on open circuit voltages.

The system thus uses a much higher quality energy than the LP steam used for regeneration in the conventional amine process. Some electrical energy will also be consumed for circulation pumps and through increased flue gas pressure drops likely similar to those for conventional amine systems. 100kJ/mole is equivalent to 2.27GJ/tonne but the thermal energy in fuel needed would equate to nearly 6GJ/tonne. (taking power plant efficiency as 40% and AC/DC conversion as 95%.) This compares rather unfavourably with the thermal requirement of the baseline amine process of 3.55GJ/tonne with prospects of this being lowered to below 3GJ/tonne through process improvements. The capital cost of providing electrical rather than thermal energy is also slightly higher as additional generating capacity is required as well as boiler capacity.

Also to be considered is the likely cost of an electrochemical cell which could be similar to that of an electrolyser. Estimates for the installed cost of electrolysers per kW vary widely but there is intense interest in the field because of the potential for energy storage through electrolysis of water to hydrogen using surplus electricity. Literature suggests cost in a wide range for example from as low as 147 to 1486 $/kW [Manage 2011], with a recent estimate from the NREL of $473/kW based on a 106MW unit costing $50.1 $million. [NREL 2011]

The costs for the electric regenerator, assuming that energy consumption could be halved to 50kJ/mol, would be that for a unit of about 170MW which would cost $85million. Compared to the base capital cost estimate for the complete capture plant of $421million this amount would not be excessive. At 100kJ/tonne this would be double and also the additional capital for the main power plant and the additional fuel consumed mean the system could not compete with the conventional process.

3.14.2. Current Status, technology readiness level and development requirements.

The electrochemically-mediated amine system has been tested at bench scale at Massachusetts Institute of Technology, Massachusetts, USA. Siemens and Topchiev Institute of Petrochemical Synthesis, Russia is also looking into this technology.

This technology is at a very early stage of development as only the basic principles and concept have been researched. It is thus assessed as at TRL-1

The mode of failure in EMAR could be oxidation due to dissolved oxygen, poor cyclic plating, or passivation, thus this shall be investigated further. The rate of degradation of the amine sorbent must also be considered. The effects of flue gas impurities, primarily sulphur dioxide (SO_2), are also a significant concern. The EMAR process needs to be tested at pilot scale for qualification of this technology.

3.15. Low temperature (cryogenic) separation of CO_2

Clodic et al 2002 has developed a process involving antisublimation/freeze-out of CO_2 on a cold surface of -83°C (see Figure 20). In this process the flue gas is cooled at around atmospheric pressure by a first cooling stage (CS1) designated as the free cooling stage. The Flue Gases (FG) cooling is done by the ambient air and two water circuits (cooling tower), one circuit exchanging energy with the flue gases, while the other exchanging energy with the ambient air. A water/water heat exchanger links these two circuits together. This arrangement isolates the process water, which comes in direct contact with the flue gases, from any contact with the ambient air. Figure 23 illustrates how the "hot" refrigerant blend enters in evaporator no.2 at a typical temperature of –50°C (the volume containing evaporator no.2 is shut). Thus during the defrosting process, the temperature and the pressure raise up to –56°C and 520 kPa. Then the solid CO_2 begins to melt and is recovered in the liquid phase by the pump.

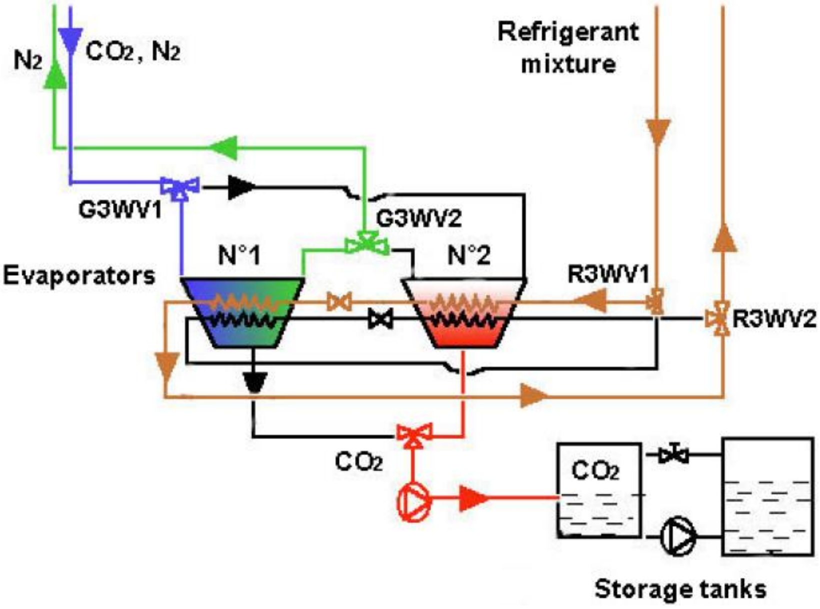


Figure 23 Layout of the low temperature CO_2 capture system [Clodic 2002]

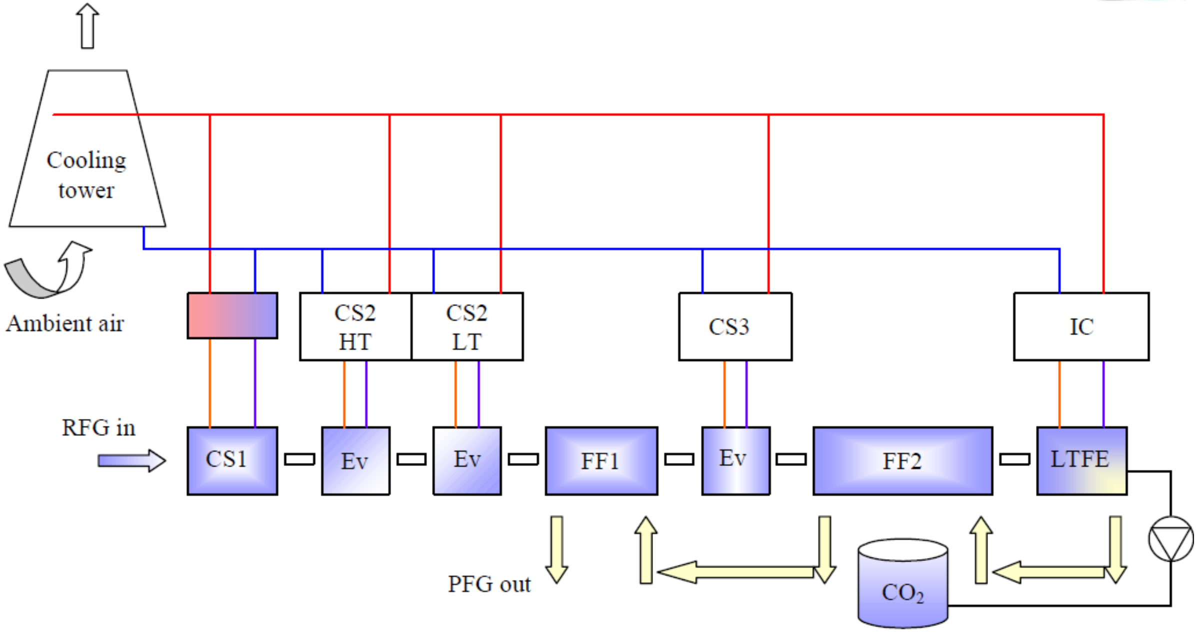


Figure 24 CO_2 capture system operational scheme [Clodic et al., 2004b]
(*CS: cooling stage; Ev: Evaporator; FF: Heat Exchanger; LTFE: Low Temperature Frosting Evaporators IC: Integrated Cascade*

Figure 24 represents the process in a cascade format. In the process a second cooling stage (CS2) brings the flue gases down to 0ºC. To achieve this temperature under all ambient conditions it was found that two successive levels of evaporating temperatures are most efficient with the lower being just above 0ºC to avoid frost. It is necessary to achieve a 1.1-4 g H_2O/kg dry FG water content for the CO_2 capture stage. Flue gases at near 0ºC have a 4 g H_2O/kg dry FG water content. Further drying would then be possible by either an adsorption or a frosting system. Calculations have shown that a frosting system is more energy efficient.

The solution was retained for the third cooling stage (CS3). The frosting temperature chosen is around -40ºC in order to design a classical simple refrigerating cycle and cut down the temperature decrease from 0ºC to -121ºC while achieving good flue gas drying; the water remaining in the flue gases at -40ºC is about 0.08 g H_2O/kg dry FG. A first heat exchanger (FF1) designed in counter current between the "Hot Flue Gases" (HFG) and the "Cold Flue Gases" (CFG) exiting the low temperature stage of the low temperature heat exchanger recovers more than 90% of the coldness of the CFG.

A second HFG/CFG counter current heat exchanger (FF2) is designed to operate between CS3 and the Low Temperature Frosting Evaporators (LTFE) in order to recover the coldness from the CFG leaving the LTFE. A special arrangement permits to frost and defrost the water content remaining in FF1 and FF2.

General Electric has also recently proposed two process options for CO_2 capture by Freeze-out. In this process recompressed and precooled flue gas is expanded in either an expander or through a nozzle.

This technology shows an energy saving when compared to that of an MEA based CO_2 capture process. Moreover the environmental impact from this technology is negligible as there are no chemicals involved. This technology is claimed to be efficient under certain conditions.

3.15.1. Energy requirement / Cost evaluation

It is reported by Clodic et al., 2002, that the total energy required by the system to capture the CO_2 and compress it to 15MPa will be 1.2 GJ/tonne CO_2 for a coal based power plant with ~14% CO_2 in the flue gas with a 90% CO_2 removal rate.

The energy consumption is critically dependent on two parameters, the amount of cold energy recovered in heat exchange of cold with hot flue-gas and the efficiency of the refrigeration cycles. The former is limited by the temperature approach which is used. Because the cold return flow of flue gas is lower than the hot feed flow the exchangers can be designed to have a close final approach but not so easily a close overall approach. The other parameter is the efficiency of the cooling cycles and here calculations were done on both a low and a high figure. The higher figure, which may be more representative of a practical application, showed 1248kJ/kg CO_2 captured as cold liquid. This would equate to 3.12GJ/kg which is competitive with amine absorption processes.

The main capital costs are for the refrigeration equipment and the heat exchangers. The cost of the refrigeration will be partly driven by the compression power. The literature did not present any cost estimates but a rough assessment can be made on the basis of the refrigeration compression power and heat exchange duty.

3.15.2. Current Status, technology readiness and development requirement.

Clodic et al 2011, have performed pilot plant tests for this technology, whereas GE have evaluated this technology on the basis of simulation work. Other companies who are involved in the development of this technology are Shell Global Solutions, Alstom and Ereie. The University of Eindhoven, The Netherlands and MINES ParisTech, France are also investigating this technology.

The equipment required for this process consists largely of refrigeration systems and heat exchangers which can be based on well-developed design and construction principles. Engineering the cyclic frosting and defrosting stages for reliable large scale operation may be a challenge and an effective solution at scale certainly needs to be demonstrated. The principles have however been validated in a small scale laboratory environment. The Technology readiness level is assessed as TRL-3 but development and commercialisation could proceed very quickly.

As the process equipment is available, a test at larger scale is the next step for this technology.

3.16. Supersonic Post-combustion Inertial CO_2 Extraction System

In the inertial CO_2 extraction system (ICES), coal-fired flue gas is directed to a converging diverging nozzle and expanded to supersonic velocities. The process of aerodynamic expansion to high velocity results in the conversion of potential energy contained in the form of pressure and temperature into kinetic energy. The rapid temperature and pressure decrease produced from this conversion results in condensation of undesirable constituents of flue gas including the desublimation of CO_2. The high density of the solid phase constituents of the flow allows for inertial separation by centrifugal forces induced by flow path curvature.

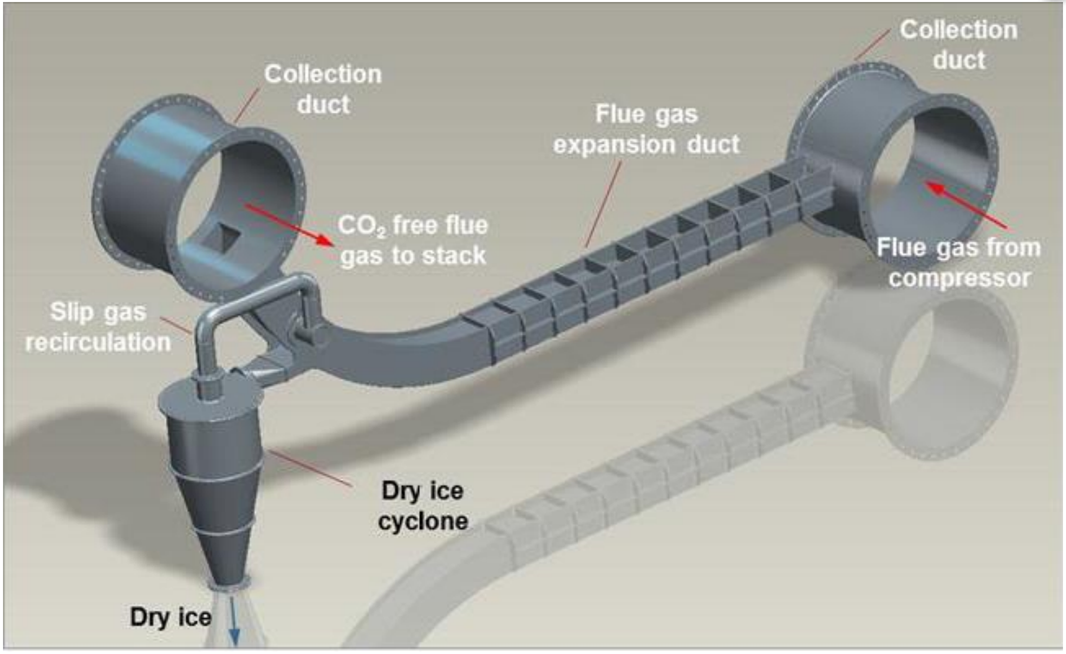


Figure 25 Configuration of an individual ICES unit [NETL]

ICES does not require external media or chemical processes such as those used with solvent or sorbent technologies, and, due to high flow velocity, is characterized by a very small system volume compared to membrane systems. ICES technology has the ability to achieve steady capture conditions very rapidly after start up. Unlike conventional technologies that require thermal conditioning of the separation media, ICES only requires a few seconds of system pre-evacuation using a steam ejector to initiate supersonic flow and be ready for service. The ICES is characterized by a footprint approximately 25 percent the size of an equivalent amine system, is readily scalable, reduces parasitic plant load from capture and compression, and includes steps for capture, purification, and highly efficient pressurization.

3.16.1. Energy requirement / Cost evaluation

A previous preliminary techno-economic analysis in DOE's project with conservative assumptions predicted the cost of CO_2 captured at $41.80 per tonne CO_2 [NETL, 2014].

The viability of this process needs careful assessment as it relies on efficient recovery of energy from the compressed fluegas stream. A similar process is offered for natural gas dewpointing by "Twister" B.V. a Dutch company spun off by Shell Global Solutions. Their process is viable when gas is already at pressure so that compression costs are avoided.

3.16.2. Current Status, technology readiness level and development requirements.

Alliant Techsystems Operations and ACENT Laboratories have teamed with the Electric Power Research Institute and The Ohio State University for further development of the technology for post combustion CO_2 capture. Previous DOE-funded research has resulted in one key remaining technical challenge: the generation of CO_2 particles greater than approximately 2.5 μm in effective diameter to ensure efficient inertial migration. Hence, the key objective of the current DOE project is verification of CO_2 particle growth to a size that permits them to migrate to a compact layer adjacent to one wall where they can be readily removed by a boundary layer capture duct. Additionally, the exhibition of efficient diffusion of the CO_2-depleted flow to atmospheric pressure is planned. A major project outcome will be confirmation of the feasibility of the inertial CO_2 separation in a compact device without any moving parts or consumables.

The principle of inertial separation using supersonic flows is proven and commercialised in another application. Although the principle is understood it is still questionable as to whether sufficiently large solid particles can be generated for it to function. This has yet to be observed. The technology readiness level is thus assessed at being in the early stage of TRL-1

A detailed laboratory-scale investigation and analysis of the mechanisms underlying CO_2 condensation, nucleation, and particle growth is required. A bench-scale testing of the complete ICES incorporating the selected particle growth method with the optimized capture duct and diffuser systems to enable the integrated testing of CO_2 condensation, migration, removal, and flow diffusion is required. An updated techno-economic analysis based on the newly developed ICES configuration and development of an environmental, health, and safety assessment for the ICES system as deployed at a pulverized coal-fired power plant are needed.

3.17. Vacuum Swing Adsorption Process (VPSA)

In this process the adsorption process takes place in a fixed bed column under low pressure. Three or more adsorption beds filled with adsorbent pellets are used. In a typical process, first adsorption takes place which is followed by applying rinse, evacuation and purge to desorb the adsorbed gas (see Figure 26). In order to have a continuous process more than one column is required. This process is mostly isothermal and adsorption and desorption take place at the same temperature, typically 40-70°C. The adsorbents are selected with high surface area, high CO_2 selectivity with lower energy requirement for adsorption.

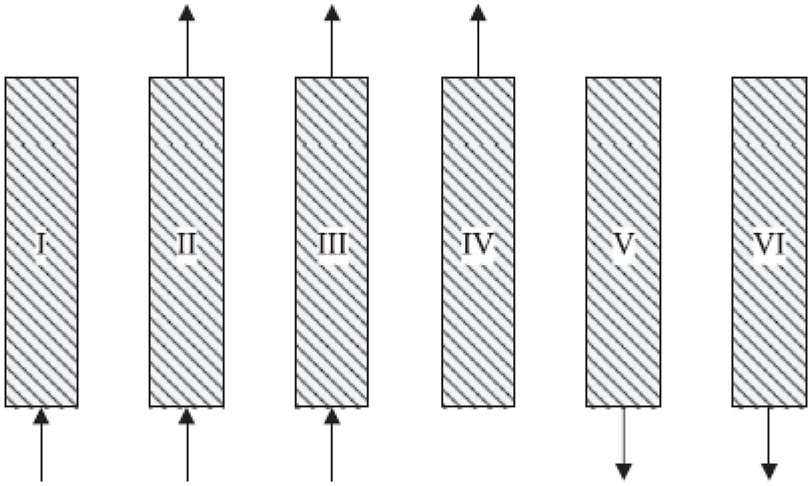


Figure 26 Six-step VSA cycle: I – pressurization, II – adsorption, III – rinse, IV – co-current blowdown, V – counter-current blowdown, and VI – counter-current evacuation [Huang et al.2013]

The VPSA process is most suitable for flue gases with a CO_2 concentration >10%. The main energy requirement of this process is from vacuum pumps, the valves and CO_2 compressors. There will be 7-8% water present in the flue gas; therefore water removal will be required to reduce the moisture level, which will require additional energy. Mostly zeolites are used in VPSA processes, however metal organic frameworks (MOFs), zeolite imidazolate frameworks (ZIFs) or other improved adsorbents with higher surface are being developed. Of particular interest are carbon based materials which are less adsorbent to water. This VPSA process has no specific environmental effect as in most cases adsorbents are stable and non-volatile.

3.17.1. Energy requirement / Cost evaluation

The CO_2 avoidance cost for vacuum swing adsorption for a 500MW pulverized coal fired power plant with 12% CO_2 in flue gas is in the range of 12-25 $/tonne CO_2 for 6 cycle steps without purge, 82-83% captured and CO_2 purity at 60-80%. For 9 step cycle with purge for 90-95% captured and CO_2 purity at 60-70%, the CO_2 avoided cost is in the range of 18-32 $/tonne CO_2 [Zhang et al. 2008].

The power consumption depends greatly not only on the properties of the sorbent but also on the design of the PSA cycle. In a study by Argawal 2010 (Carnegie Mellon) various cycles for post combustion CO_2 capture were simulated and one designed to minimise power consumption predicted an energy consumption of 465kWh/tonne (1.67GJ/tonne). This is as work and, assuming a 40% power plant efficiency, would equate to 4.2kJ/tonne thermal which is considerably higher than for solvent absorption. The ability of such systems to significantly lower the additional cost of electricity needs to be critically assessed as only with highly energy efficient cycles and good selectivity is it likely that they will compete. Although low costs are quoted in the literature these may be overly optimistic.

3.17.2. Thermodynamic considerations

This separation method applies work in the form of compression energy to desorb the CO_2 from the adsorbents. The equilibrium partial pressure from which the CO_2 has to be pumped will be that to which the sorbent has been exposed. In addition the energy of adsorption will also have to be supplied. Promising materials based on carbon have been identified and have isosteric energy of adsorption of about 25kJ/mol which is equivalent to about 0.57 GJ/tonne as work or 1.4 GJ/tonne thermal input assuming 40% power plant efficiency. However most of this energy does not have to be supplied in a cyclic adsorption process for the following reason. On adsorption the heat of adsorption will slightly raise the temperature of the sorbent. On desorption the reverse effect will occur, in effect the captured gas is "evaporating" from the surface sites and the sorbent cools, the binding energy is thus recovered. However the temperature change will result in a change in the adsorption isotherm so that a slightly lower pressure will be needed to desorb the gas. This will in turn slightly increase the vacuum pressure which needs to be applied and thus the compression energy consumption.

In practice a lower than equilibrium pressure has to be used to provide an adequate driving force. The theoretical minimum work will thus be that for the same separation using a staged membrane process. Additional losses are incurred due to the depressurisation and re-pressurisation process. The VPSA process thus theoretically has potential to deliver similar performance to a membrane system provided a suitably selective adsorbent is found.

3.17.3. Current Status, technology readiness level and development requirements.

Currently there are two pilot plants for VPSA, one in Australia and a second in Shanghai, both plants have three columns. The column diameter is 0.2 m and height is 1 m in the Shanghai plant. In this plant continuous operation has been performed for 15% CO_2 in flue gas from coal fired power plant, capturing 79% CO_2 at a rate of approximately 12kg/h of CO_2. The captured CO_2 purity is 85%.

The major engineering companies such as Air products, Linde and UOP are setting up PSA plants, and a small scale adsorption process is being developed by Wärtisilä Hamworthy (Norway). Adsorbents such as zeolites have been developed by UOP, Grace and Zeolyte. SINTEF and the University of Oslo also have activities in development of improved adsorbents and an adsorption process is developed by SINTEF as well.

The principles of VPSA are well proven but applications to CO_2 capture have only been demonstrated at very small scale. Furthermore a sorbent with the desired properties for economic commercial operation has yet to be developed. It is thus considered that while the concept is proven much still needs to be validated for a commercial system. It is thus assessed at TRL-3.

VPSA process is required to be demonstrated at large scale as well as producing higher purity CO_2, at least 95%, in order to be suitable for transport by CO_2 pipeline. Further improvements in the adsorbents' stability against impurities and increased CO_2 adsorption capacity are required.

3.18. Temperature Swing Adsorption (TSA)

In this process CO_2 is adsorbed at low temperature (typically 40-60°C) and CO_2 loaded adsorbent is transferred to another section where at high temperature (typically 80-150°C) CO_2 is desorbed. Alternatively absorption and desorption can be performed in the same column by first absorbing CO_2, followed by heating to desorb CO_2. TSA requires multiple columns in order to operate continuously. In the TSA process the heat transfer is very important as well as low pressure drop across the adsorption bed. TSA technology does not have significant environmental impacts as the adsorbents used in this process are non-volatile and stable.

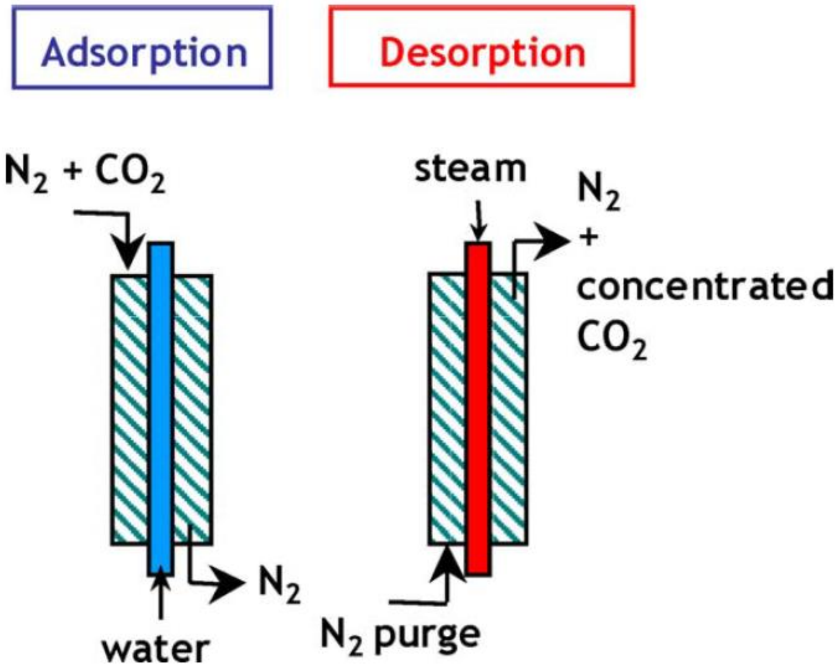


Figure 27 Two-step indirect TSA cycle [Clausse 2011]

TSA technology has been proven by experiments under real flue gas conditions. Another alternative process which can rapidly increase the temperature of the adsorbent is Electric

Swing Adsorption (ESA), where a low voltage electric current is employed to heat the adsorbent by the direct Joule effect. One disadvantage of ESA when compared to TSA is that in ESA the temperature increase is achieved by using electric power while in the case of TSA low-grade heat is employed.

3.18.1. Energy requirement / Cost evaluation

Grande et al. 2008 evaluated the cost of CO_2 capture using an ESA process. They estimated the energy consumption associated with the separation of CO_2 to be 2.04 GJ/tonne CO_2, for an adsorbent consisting of 70 wt.% zeolite X and 30 wt.% of a conducting binder. This rather high figure as electric energy almost certainly makes this process uneconomic

Regeneration using thermal energy is thus more likely to be of interest. The energy consumption is discussed below and there are indications that it could be slightly superior to the conventional amine absorption process. However the potential reduction being only around 10% suggests that cost reduction due to better energy efficiency might only be 5% of the benchmark increase. There may be more scope for cost reduction in the process equipment but this cannot be assessed until more detailed schemes are assessed and decisions on bed type, cycles, cycle times etc. have been made.

3.18.2. Thermodynamic considerations

The temperature change required to achieve regeneration will increase as the free energy of adsorption increases. A high energy of adsorption will in turn result in higher loading for a given partial pressure of CO_2. It will not be efficient to use heat to regenerate if most is not recovered because of the relatively high heat capacity of the sorbent as compared to that of the adsorbed CO_2. An issue is the method by which heat is transferred in and out of the adsorbent beds in an efficient manner. Direct heating using a gas flow requires very large flows because of the low heat capacity of appropriate gases. Thus despite the complexity of arranging indirect heat transfer to either fixed or fluidised bed this method may be the more practical. Using fixed beds it is possible to attain much higher CO_2 loadings than with fluidised beds because the feed gas can be allowed to flow until the entire bed is saturated at the partial pressure of CO_2 in the inlet. In a fluidised bed the equilibrium will be close to that of the gas at the outlet because of the intense mixing. For 90% capture this would thus be $1/10^{th}$.

The thermodynamics and energy consumption of the TSA process are examined in some detail in a paper by Pirngruber [Pirngruber 2013]. The lower limit for energy consumption in a fixed bed TSA was predicted to be as low as 2.1GJ/tonne thermal but this is subject to several optimistic assumptions including finding a sorbent with a higher capacity for CO_2 than currently known and employing isothermal conditions in the adsorber necessitating installation of a very large heat transfer area. More realistic predictions would suggest the limit to be no lower than 3.2GJ/tonne thermal. Fluidised bed systems are considerably more energy intensive and cannot compete. Thus the overall energy consumption would be only slightly lower than the benchmark 3.55GJ/t thermal, which equates to 1.19GJ/tonne as work excluding compression energy but including electrical auxiliaries for the capture process. This would equate to about 1.09GJ/tonne as work assuming similar auxiliary load. Note that this refers to amount captured. In practice it is the amount abated which is of interest and benchmark performance studies indicate overall figures including compression of around 1.57GJ/tonne.

3.18.3. Current Status, technology readiness level and development requirements.

There is only one large pilot plant in operation since 1990 for a dual PTSA (PSA/TSA) process reported at Tokyo Electric Power Company. The inlet flue gas flow rate is 1000Nm^3/h with ~15% CO_2 in the flue gas. This results in 265kg CO_2/h on the basis of a 90% CO_2 capture rate. In this plant Ca-zeolite is used as an adsorbent.

Companies such as ARI (USA) and Inventys (Canada) have patents for a moving bed concept and a Monolith concept respectively. Still there is no existing large scale demonstration of these technologies. Several academic groups are working on development of high-surface area adsorbents for post combustion capture usage e.g. ETH (Switzerland).

The principles of TSA are well understood but formulation of an application likely to be competitive in energy consumption, practicality and cost has yet to be achieved. Certainly a sorbent with adequate performance and properties has yet to be found. The Technology readiness level is thus assessed as TRL-1

Improved adsorbents with higher surface area and stability are required to be developed further. As well, moving bed concepts for TSA could also be developed further and tested in real pilot plant operation.

3.19. Post Combustion Capture Technologies for Non-Power Industries

Many of these future technologies are at the proof of concept and pilot plant evaluation stage. Hence, focus of these technologies’ suitability is more for power generation emission sources. However, there are some technologies which are reported in the literature to be suitable for industrial application as described below.

Precipitating solvent

TNO has evaluated its precipitating solvent process based on amino acid salts (DECAB) on refinery flue gas with 8% CO_2 concentration [Fernandez et al 2011]. The specific heat duty of this process is reported to be 2.8 GJ/tonne CO_2, which is considered to be lower than the existing process for CO_2 capture from flue gas with low CO_2 concentration.

EMAR

Electrochemically-mediated amine regeneration (EMAR) systems are more versatile and can be applied to other industries, such as cement, steel, and aluminium, where large amounts of low pressure steam are not readily available for solvent regeneration. EMAR systems may also be effective for smaller-scale applications such as producing CO_2 for bio-refineries.

Polymeric Membrane

Membrane processes are suitable to be applied in the iron and steel industry and possibly the cement industry where the CO_2 concentration in flue gas can be in the range of 23-36%. CO_2 separation in the natural gas industry by use of polymeric membranes is a well matured technology.

3.20. Conclusions - Post combustion technologies

Currently there are several post combustion capture technologies under development. Table 7 represented IEAGHG’s preliminary evaluation of the above mentioned new technologies on the basis of their CO_2 avoidance cost, energy requirement, material cost and environmental impact. This evaluation was performed on the basis of available information in the literature.

Based on the evaluation presented in table 7, it can be noticed that the cost of CO_2 capture is claimed to be lowered by these future technologies as well as their environmental impact. However more work is required to characterise the environmental impact of some of these future technologies.

A more critical assessment of the costs and energy performance of technologies has been made since the first assessment. In most cases this has led to a more conservative view of the potential and identifies several technologies as unlikely to compete. The assessments have been summarised in tables in the executive summary and for post combustion capture the assessment is shown in table 8 below.

In addition to the consideration of individual technologies it has also been identified that there may be interesting options to develop hybrid systems based around the recycling of CO_2 to the power plant boiler using the combustion air as a sweep gas. Although this has been proposed initially using a membrane separation it is in fact amenable to use by solvent and solid adsorption systems. Furthermore whilst the primary separation stage for the CO_2 enriched flue gas has been based on membranes all separation technologies could be used in this location in the process. Evaluation of all possible combinations would have to be done to identify which of them warranted further development. This hybrid scheme causes flame temperatures in the power generation process to fall. However this does not reduce cycle efficiency because the full combustion temperature cannot be used. This available exergy is thus utilised to drive part of the capture process. This advantage appears to similar to that derived by some of the high temperature solid looping processes which are able to reject heat at temperatures above those of the working fluid thus avoiding efficiency losses in the power generation cycle.

Table 7 Preliminary evaluation of future generation post combustion capture technologies

Technology	CO_2 avoidance cost*	Energy requirement*	Material/Solvent Cost*	Environmental Impact*
Precipitating Solvent	Reduce by Half	Low; << 3 GJ/tonne CO_2	Low	Low
Two phase liquid solvent	25% lower	Low; <2.5 GJ/tonne CO_2	Low	Unknown
Ionic liquids	High	Low; approximate 16% lower*	High	Low
Gelled Ionic Liquid-Based Membranes	Low	Low	Medium-High	Unknown
Enzyme activated solvent	Medium	Low; approximate 33% lower	Low	Medium
Algae based CO_2 capture	Medium	Low	Low	Low
Electrochemically-mediated amine	Medium	Medium	Low	Similar
Supersonic Inertial CO_2 extraction	Low	Low	Low	Unknown
Vacuum Swing Adsorption	Low	Low; 30-50 kJ/mole CO_2	Low	Low
Temperature Swing Adsorption	Low	Low; 2.04 GJ/tonne CO_2	Low	Low
Polymeric membrane	Low	Low	Medium	Low
Low temperature separation	Low	Low; 1.2GJ/tonne CO_2	Medium	Low
Polymeric membrane & low temp. separation	~23% lower	Low	Medium	Low

Notes: *compared to a conventional solvent Monoethanolamine (MEA) based process

Table 8 Assessment of Technology Readiness Levels and LCOE reduction prospects – Post-combustion

Technology	TRL	LCOE increase reduction prospects
Benchmark proprietary MEA	9	LCOE increase expected to be about 100% of baseline
Improved conventional solvents	6-8	Incremental reductions possible
Encapsulated solvents	1	Potential still to be proven
Precipitating solvent	4-5	5-10%
Biphasic solvents	4	16%
Ionic liquids	1	No viable process yet
Polymeric membranes	6 (fast development possible)	30%
Polymeric membrane/cryogenic separation hybrid	6 (fast development possible)	Similar or better than polymeric membrane alone
RTIL membranes	2	Could be similar or better than polymeric membranes
Enzyme catalysed adsorption	1	7% Incremental reduction due to reduced absorber size
Algae based capture	1	Unlikely in foreseeable future
Electrochemically mediated absorption	1	High electrical energy consumption makes reduction unlikely
Cryogenic capture	3 (rapid development possible)	Moderate reduction possible if favourable assumptions are valid
Supersonic inertial capture	1 (early stage of)	Too early to validate
VPSA	3	Relatively high energy requirement makes significant reduction unlikely
TSA with thermal regeneration	1	Uncertain
TSA with electric regeneration	1	Likely much higher

With regard to the future improvements for these technologies, further development in improving the material, process design and integration is important. Large scale pilot plant testing (>10MWe) is also important to further improve and build confidence in these technologies. Figure 28 below illustrates the key areas of further work for these future generation post combustion capture technologies.

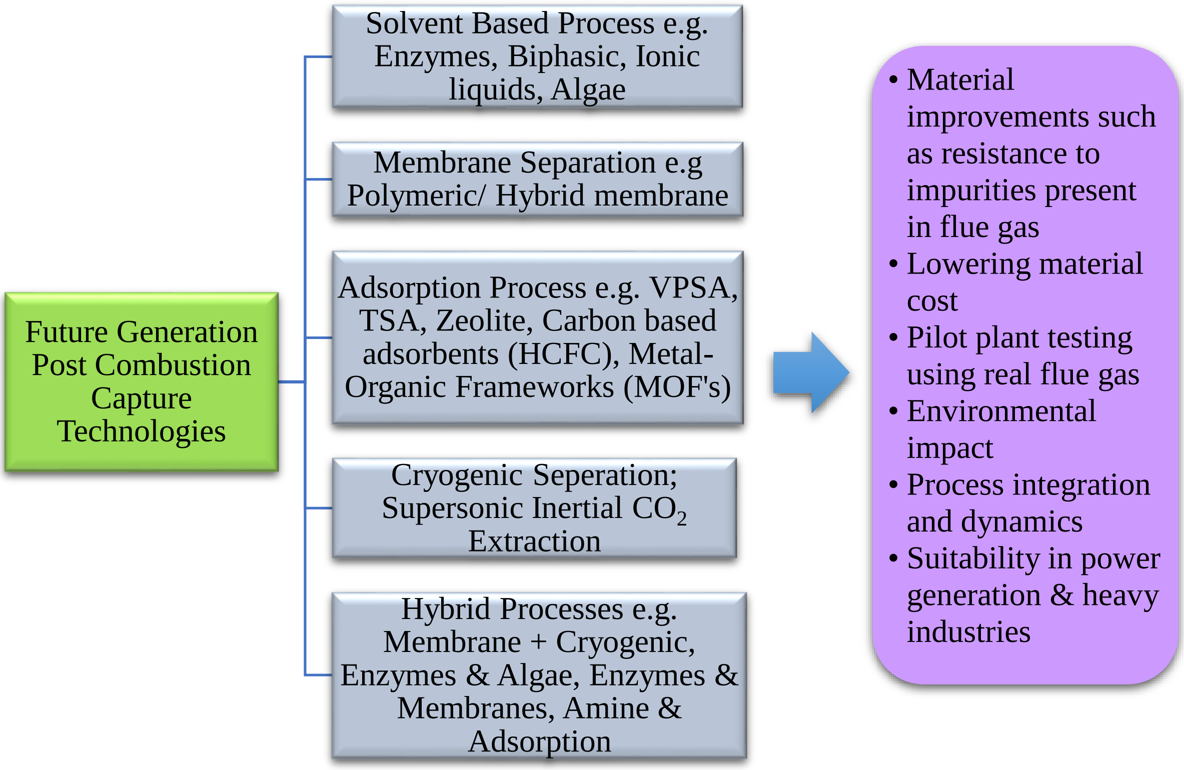


Figure 28 Evaluation required for future generation post combustion capture technologies.

4. Pre-Combustion Capture Technologies

In pre-combustion capture, fuel is reacted with oxygen or air, and in some cases steam, to give mainly carbon monoxide and hydrogen in processes known as gasification, partial oxidation and reforming. The mixture of mainly CO and H_2 is passed through a catalytic shift conversion reactor where most of the CO reacts with steam to give CO_2 and more H_2. Most of the CO_2 is separated and the H_2 can be used as fuel in a gas turbine combined cycle plant. The process is in principle the same for coal, oil or natural gas, but when coal or oil are used there are more stages of gas purification to remove particles of ash, sulphur and nitrogen compounds and other minor impurities. For solid fuels this overall process is called Integrated Gasification Combined Cycle (IGCC). Hydrogen produced in plants with pre-combustion capture can also be used as a decarbonised energy carrier for distributed energy consumers such as transport, domestic and commercial building, small scale industry and some large energy consuming industries such as oil refining. As hydrogen is easier to store than electricity, it can be more suitable for satisfying distributed heat demands, which have high daily and season variations in demand. Stored hydrogen from pre-combustion capture plants could also be attractive for decarbonisation of intermediate and peak load power generation.

The conditions for CO_2 separation in pre-combustion capture processes are substantially different from those in post-combustion capture processes. The feed to the CO_2 capture unit in a coal-based IGCC process, located upstream of the gas turbine, would have a CO_2 concentration in the range of 15-60% and a total pressure of 2-7 MPa [IEAGHG, 2014; IEAGHG, 2005]. The CO_2 partial pressure is therefore up to 1000 times higher than in post-combustion capture. This enables solvents with lower energy consumptions to be used such as the physical solvent processes Rectisol (cold methanol) and Selexol (dimthylether of polyethylene glycol). Another advantage is that these solvents can release some of their CO_2 at elevated pressures, which reduces the energy consumption and cost of CO_2 compression. The physical solvents can also selectively separate sulphur compounds, mainly H_2S, from the hydrogen-rich gas before it is fed to the gas turbine.

Several integrated gasification combined cycle (IGCC) plants without CO_2 capture, using coal and petroleum residues, are already operational [Higman, 2013]. The technologies for gas production and CO_2 separation are already proven in ammonia production and other industrial processes, especially in large modern coal gasification chemical production plants in China. Currently no IGCC plants with large scale CO_2 capture are in operation but a 524MWe lignite gasification plant at Kemper County, USA which has a 65% capture rate is scheduled to start-up in 2016.

The optimum technologies for pre-combustion capture in natural gas fuelled plants may be different to those in IGCC, because for example the partial pressure of CO_2 is lower, which improves the attractiveness of chemical solvents versus physical solvents. An alternative technology is vacuum swing adsorption, which is being used for pre-combustion capture at a commercial scale hydrogen plant at Port Arthur in Texas. This DOE funded project captures 1Mt/y of CO_2.

The energy consumption for CO_2 separation is less than in post combustion capture, for the reasons described above but there are other significant energy efficiency losses in IGCC which do not apply to post combustion capture:

- Steam has to added to the feed to the shift converter, which is provided either by addition of externally generated steam or by quenching the gasifier product gas, thereby reducing the amount of steam that would be generated in a heat recovery boiler. The surplus steam in the shifted fuel gas usually has to be condensed upstream of the CO_2 separation unit, and the energy from cooling and condensation is only available at low temperatures.
- Shift reaction is an exothermic process and although the heat of reaction can be used to raise high grade steam this is less efficient than feeding the energy to the gas turbine combined cycle plant.
- Removal of CO_2 from the fuel gas reduces the mass flow through the expansion part of the gas turbine, thereby reducing the power output. In practice the removal of CO_2 is usually offset by the addition of more compressed nitrogen or air. The power consumption for the nitrogen or air compression is significant.
- The gas turbine firing temperature may have to be reduced because burning a high hydrogen fuel gas results in a higher steam concentration in the gas flowing through the gas turbine, which increases heat transfer to the blades. This has to be offset by a lower turbine inlet temperature, which reduces the gas turbine efficiency.

When considering new technologies to reduce the energy consumption for pre-combustion capture in IGCC it is necessary to take a holistic view including interactions with the other parts of the process such as gasification, fuel gas desulphurisation, shift conversion, CO_2 compression and the power generation process.

The capital costs of pulverised coal plants with and without capture and an IGCC plant with capture are shown in Figure 29 [IEAGHG, 2014b]. It can be seen that the cost of the capture unit in the IGCC plant is substantially lower than the cost in the pulverised coal plant (even though the ‘capture’ unit in the IGCC plant also removes sulphur compounds from the fuel gas). However the overall cost of the IGCC plant is higher than that of the pulverised coal plant with capture, because of high costs for other parts of the plant. However the costs of all of these technologies are subject to significant uncertainty until full scale commercial plants have been brought into service and consequently the relative costs of the different technologies may change.

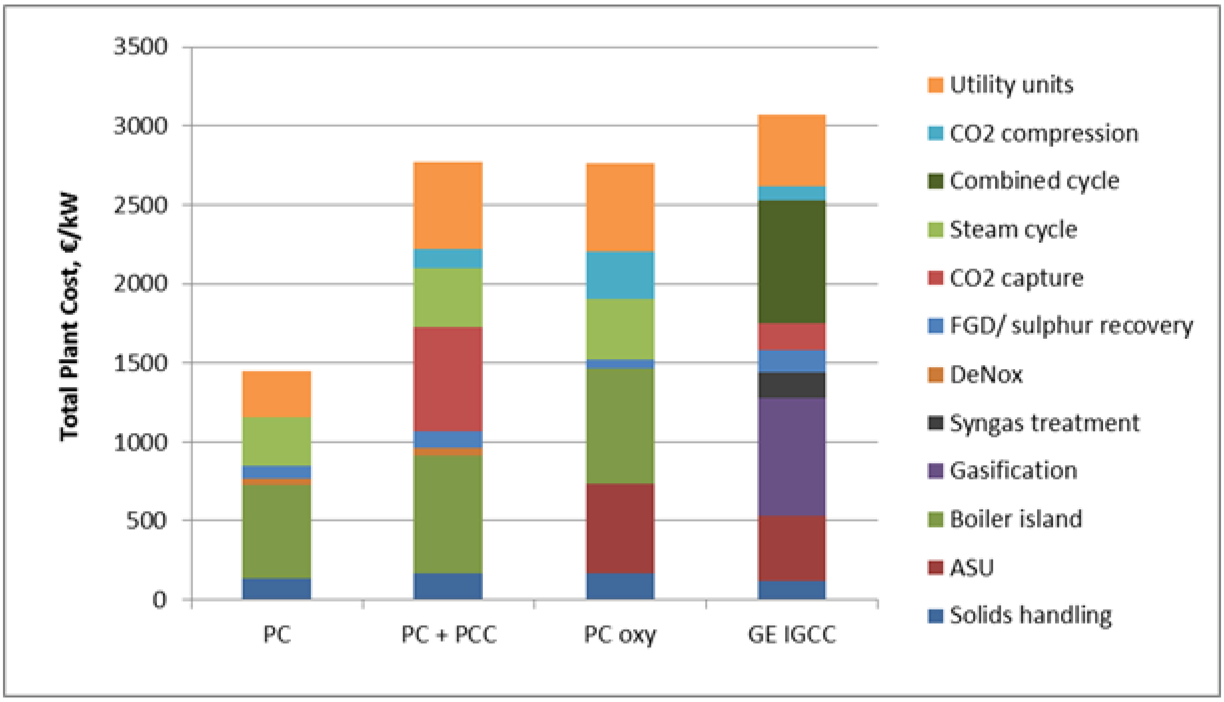


Figure 29 Specific Total Plant Costs of power plants with and without CO_2 capture

The costs of adding CO_2 capture to an IGCC plant have also been explored in detail by NETL [NETL 2013]. Analysis of the cost breakdown reveals that about 17% of the increased cost of electricity can be attributed to the capital cost of the shift reactors and extension of the Selexol unit from one stage (for sulphur compound removal) to two stage. The rest of the increase, about 87% is attributable to the loss of efficiency resulting in consumption of more fuel and a higher capital charge for the base plant per unit of net output. Hence improvements in LCOE for IGCC with capture need to focus on efficiency and furthermore there is opportunity for favourable trade off between efficiency gains and more expensive capture plant.

For post combustion capture, the main focus on cost reduction is on reducing the energy consumption and capital and operating costs of the CO_2 capture unit itself, as that is the main contribution to the overall cost of capture. To substantially reduce the cost of IGCC with capture not only should the cost of capture be reduced but also the costs of the other process units associated with capture such as shift conversion and the interaction between these units and the gasification, power generation and CO_2 compression units should be improved. Reductions in the costs of gasification, air separation and power generation units would also help to improve the competitiveness of IGCC with CO_2 capture. Improvements to oxygen production technology are described in the oxy-combustion section of this report. Improvements are being made to gas turbine combined cycles and thermal efficiencies are expected to continue to improve in future, but discussion of these improvements is considered to be largely outside the scope of this study. A particular issue at present for IGCC is that gas turbine vendors are not willing to offer their most modern highest efficiency gas turbines for combustion of high hydrogen content fuel gas in IGCC. Overcoming this constraint could provide a significant improvement to IGCC efficiencies and costs. Although this report does not consider improvements in gas turbines it does consider an alternative higher efficiency power generation technology, namely fuel cells, because this can include integrated CO_2 capture.

This report focusses on technologies which are in early stage development which offer the potential for substantial reductions in costs of electricity for plants with pre-combustion capture, namely gas separation membranes, sorbent enhanced water gas shift, low temperature removal with and without CO_2 recycle and solid oxide fuel cells with CO_2 capture.

4.1. Gas Separation Membranes

4.1.1. Description and status

Gas separation membranes rely on differences in physical or chemical interactions between gases and a membrane material, causing one component to pass through the membrane faster than another. Various types of membrane are currently available for pre-combustion capture, including porous inorganic membranes, palladium membranes, polymeric membranes and zeolites. Membranes are used commercially for CO_2 removal from natural gas at high pressure but development is required before membranes could be used cost effectively on a large scale for pre-combustion capture of CO_2 in power plants.

Pre-combustion capture membranes can be classified as hydrogen membranes in which hydrogen selectively passes through the membrane, and CO_2 membranes, in which CO_2 selectively passes through the membrane. There is a range of options for configuring membranes for pre-combustion caption capture, e.g. before shift conversion, between shift reactors, within shift reactors or during CO_2 compression [NETL, 2009]. An important issue is to match the operating temperature of the membrane to its location with an IGCC plant, as shown in Figure 30.

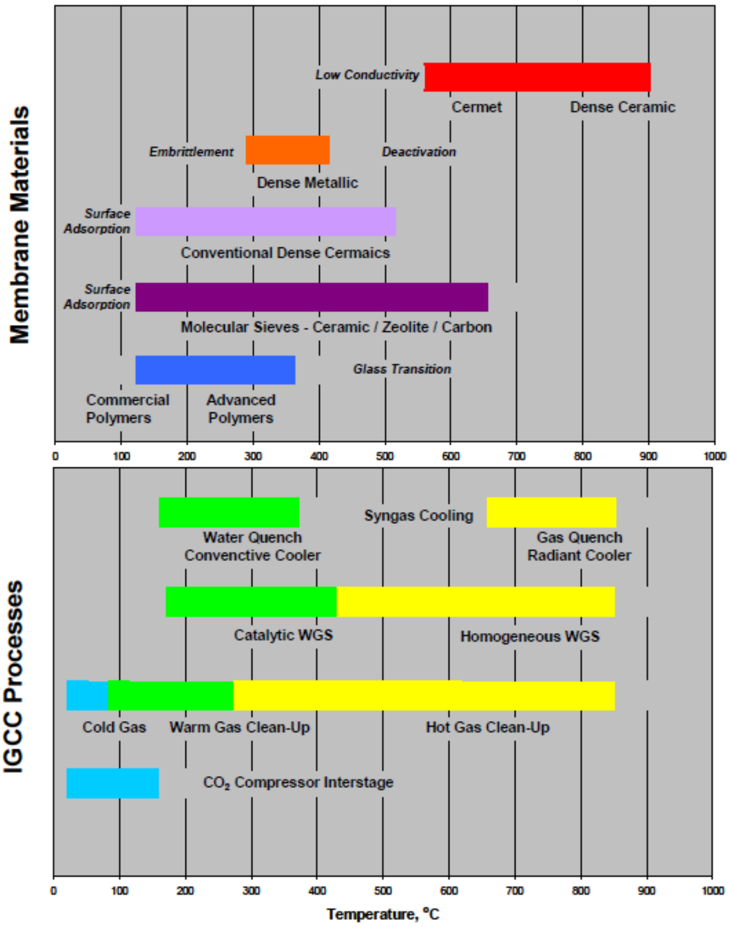


Figure 30 Temperature match for membrane IGCC integration [NETL, 2009]

Membranes can be combined with methane reforming or partial oxidation and/or water gas shift reaction. The removal of hydrogen from the reaction zone by the membrane pushes the reaction equilibrium towards production of hydrogen, resulting in a higher degree of conversion and possibly a lower steam requirement.

$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$ (Methane partial oxidation)
$CH_4 + H_2O \rightarrow CO + 3H_2$ (Steam reforming)
$CO + H_2O \rightarrow CO_2 + H_2$ (Water gas shift reaction)

Similar advantages can be achieved by sorbent enhanced water gas shift and methane reforming reactors, which are described later in this report.

4.1.2. Metallic hydrogen separation membranes

Metallic membranes are generally based on palladium or palladium alloys although it is possible to use various metals. As shown in Figure 31, hydrogen separation is achieved by dissociative chemisorption of hydrogen on the surface producing atomic hydrogen which diffuses through the metal lattice to the opposite side of the membrane. There the atomic hydrogen recombines to H_2 and diffuses away from the surface. In most cases the membrane consists of an inorganic support covered with a thin layer of precious metal, which is normally palladium or palladium alloy, although other metals can be used [Scholes, 2010].

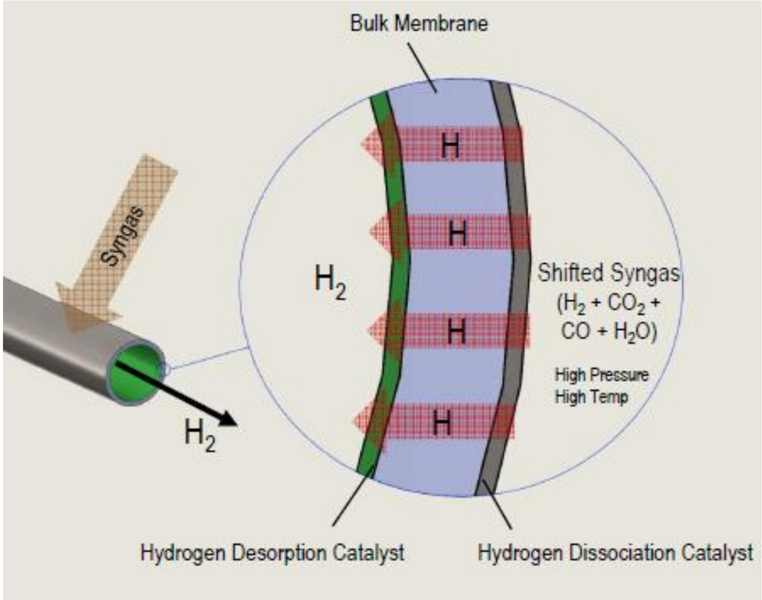


Figure 31 Metallic hydrogen separation membrane [Jack, 2011]

The system results in hydrogen on one side of the membrane and a high pressure stream of CO_2 with a small amount of CO and other impurities on the other side of the membrane. The high pressure of the CO_2 minimises the energy consumption for CO_2 compression. The hydrogen is in principle almost pure because no other gas undergoes dissociation at the metal surface, although microscopic holes in the membrane can permit other gases to pass through, leading to a reduction in selectivity. The flux of hydrogen is proportional to the square root of the partial pressure difference across the membrane. If the hydrogen is to be used in an IGCC gas turbine, nitrogen sweep gas can be used to reduce the hydrogen partial pressure on the hydrogen side of the membrane (nitrogen has to be added to the hydrogen feed to a gas turbine anyway). If pure hydrogen is required the membrane can be operated with a greater absolute pressure difference.

Metallic hydrogen separation membranes normally operate at elevated temperatures, e.g. around 280-440°C [NETL, 2011c]. Metallic membranes can be used in combination with conventional cold solvent desulphurisation, such as Selexol or Rectisol, but the advantage of membranes would be maximised if they were used in combination with warm gas desulphurisation operating at similar temperatures to the membranes. This avoids the costs and energy losses associated with cooling the gas from the gasifier down to a low temperature and condensing the steam included within it. Avoiding condensation of the steam provides addition gas for expansion through the gas turbine. NETL is funding a warm gas desulphurisation plant to process a side-stream of about 20% of the fuel gas flow at Tampa Electric’s 250MWe Polk IGCC plant in Florida. This plant based on RTI’s technology uses recirculating zinc oxide solid sorbent to remove more than 99.9% of the sulphur contaminants from gasifier fuel gas. The resulting zinc sulphide is converted back to zinc oxide and SO_2 by combustion with oxygen in a separate reactor [RTI, 2014. The plant started-up in April 2014.

A disadvantage of hydrogen separation membranes is that the CO_2-rich gas contains relatively high concentrations of impurities. Catalytic oxygen-blown combustors can be used to react the CO and un-separated H_2 to CO_2 and steam. Non-condensable impurities such as nitrogen could if required be removed using low temperature separation, as is used for processing the CO_2-rich gas from conventional oxy-combustion CCS but this would be an additional cost and efficiency penalty. Gasifiers which do not use nitrogen for fuel pressurisation and feeding would be advantageous for combination with hydrogen separation membranes. Gasifiers which can operate at higher pressures such as slurry feed gasifiers, would have the advantage that it may be possible to avoid the need to compress the hydrogen-rich gas before or after the membrane.

Another disadvantage of palladium membranes is the effect of impurities. Pure Pd membranes have no tolerance to sulphur and are destroyed by large lattice expansion when Pd-S is produced. However a small degree of tolerance, e.g. up to 1-2 ppm, can be achieved by use of Pd-alloys [Grazzani, 2014]. Pd is also susceptible to CO, NH_3 and chlorine, all of which exist in pre-combustion syngas streams [Scholes, 2010]. Pd membranes currently have short lifetimes, and the cost of periodically replacing them in a commercial plant would be high.

4.1.3. Porous inorganic hydrogen separation membranes

Porous inorganic membranes can also be used to separate hydrogen from syngas. Materials that have been used include zeolites, silica, alumina, nitrides and oxides. The materials have carefully controlled pore structures to enable hydrogen molecules to pass through while larger molecules are retained. Alternatively larger pores can be used and separation is achieved by Knudsen diffusion. Important criteria for porous inorganic membranes are selectivity, diffusion rate and tolerance to impurities. Surface treatment to improve the sorption of H_2 to the pore walls can improve selectivity by increasing the rate of migration along the pore walls, in a process called surface diffusion [Scholes, 2010].

4.1.4. Carbon hydrogen separation membranes

Carbon membranes act as molecular sieves as well as allowing surface diffusion. They are typically prepared by high temperature pyrolysis of organic polymers. In common with silica membranes their performance can suffer in the presence of high levels of water vapour. Carbon nanotubes have also been suggested as membranes but high cost would currently be an issue.

4.1.5. Dual stage hydrogen separation membrane schemes

A dual-stage membrane-reactor approach is being developed by MPT. Hydrogen-selective carbon molecular sieve (CMS) membranes accomplish warm gas clean-up of coal derived syngas, water gas shift reaction and bulk hydrogen separation in a single unit. Co-Mo catalysts is used for the shift reaction. The CO_2-rich gas is than passed through a cold gas cleaning unit and the clean gas, containing around 82% CO_2 and 11% H_2, is compressed and fed to Pd membranes which recover the hydrogen. Although the selectivity of the CMS membrane is not as high as competing polymeric and metallic (Pd-based) membranes the CMS membranes are inert and robust

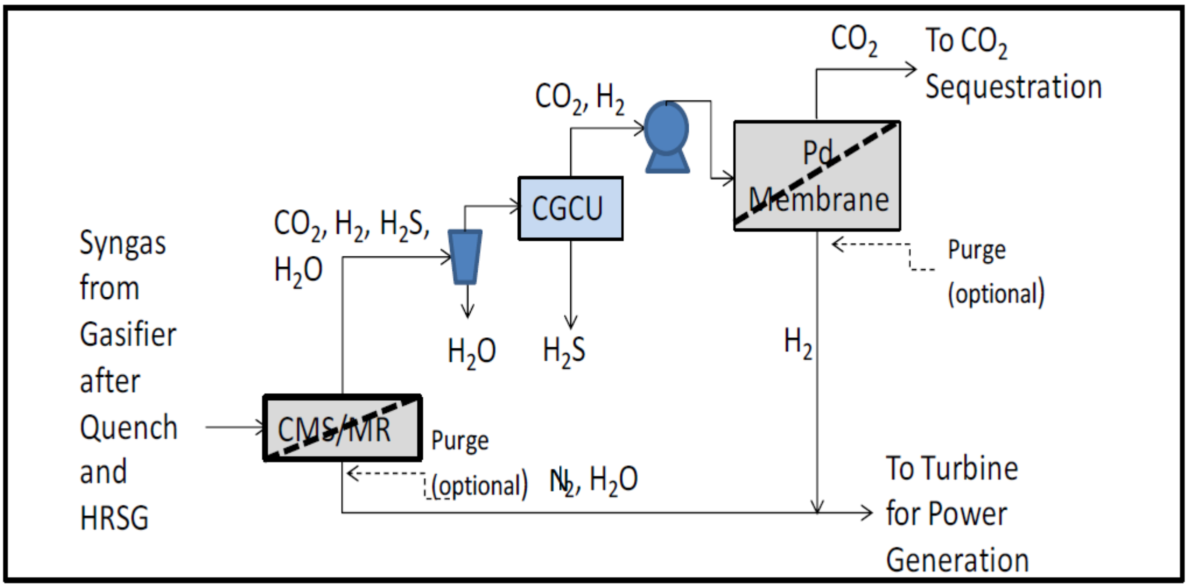


Figure 32 Dual-stage membrane reactor

4.1.6. *CO_2 separation membranes*

The development of membranes that will retain the small molecular size of H_2 but permeate the larger CO_2 molecules is reported to be a significant challenge [Scholes, 2010]. It is important that the solubility selectivity strongly favours CO_2 and that the diffusivity selectivity, which favours H_2, is minimised. The favoured option is polymeric membranes and a wide range of polymeric materials have been considered [Scholes, 2010]. The selectivity of such membranes is limited and CO_2 recoveries are typically 50-80% and the CO_2 purity is up to 95% [MTR, 2014].

4.1.7. *Energy requirement / cost evaluation*

NETL has undertaken a detailed assessment of the performance and costs of IGCCs with warm gas cleaning and hydrogen separation membranes [NETL, 2010] and the results are summarised in Table 9. The cost assessment is based on NETL's 2015 target flux and temperature for the membrane. The efficiencies and costs are shown relative to a baseline which is includes an advanced "F" class gas turbine and a dry feed entrained flow gasifier. In the baseline plant the fuel gas from the gasifier is fed to a sour shift reactor and then to a 2-stage Selexol unit. In the warm gas cleaning cases the gas is fed to a warm gas desulphurisation unit similar to that being employed at the Polk IGCC plant, followed by a clean shift and then either a single stage Selexol unit or hydrogen membranes.

Table 9 Performance and costs of plants with warm gas cleaning and H_2 membranes

	Difference compared to conventional IGCC	
	Warm gas cleaning and Selexol	Warm gas cleaning and hydrogen membrane
Efficiency, % points (LHV)	+0.8	+3.0
Efficiency, % (LHV)	+2.5	+11.4
Capex per kWe, %	-2	-17
Levelised cost of electricity, %	-1.4	-13.2

The cost differences are dominated by the differences in thermal efficiency, and hence fuel cost, and capex. The cost of chemicals is higher in the warm gas clean-up cases due to the cost of zinc oxide sorbent make-up and there is an operating cost allowance for membrane replacement, but these costs are of relatively small significance overall. The NETL assessment is based on a gasifier operating at about 70MPa, which favours a membrane plant because the hydrogen would be produced at a pressure suitable for feeding directly to a gas turbine. If the gasifier operated at a lower pressure, typical for a dry feed gasifier, a hydrogen compressor would be needed. The high operating temperatures of membranes would result in a relatively high compression power consumption.

The thermal efficiency of an IGCC plant using the dual stage membrane reactor process shown in Figure 32 is estimated to be 2 percentage points higher than that of a plant with CO_2 capture using a conventional 2-stage Selexol process and the LCOE is predicted to be \$95/MWH compared to \$106/MWh for the Selexol based plant and cost of CO_2 avoided relative to an IGCC without capture is \$25/t CO_2 compared to \$42/t for a Selexol-based plant with capture [Liu, 2013].

4.1.8. Current Status, technology readiness level and development requirements.

Tests of various types of membrane (polymeric, carbon-based and palladium hydrogen separation membranes and a polymeric CO_2 separation membrane) have been carried out using a slip stream of gasifier fuel gas at the National Carbon Capture Centre (NCCC) at Wilsonville, USA [Wu, 2013].

MTR’s polymeric CO_2 separation membrane is being tested at a 225kg/h pilot plant at the NCCC, using syngas from a transport gasifier. MPT’s membrane reactor system is being tested at a 23kg/h scale pilot plant at the same site and MTR and WPI are testing hydrogen membranes at a 5kg/h scale [Wu, 2013].

A 20 Nm^3/h pilot plant to test membranes from various suppliers has been built by Tecnimont-KT at Chieti Scalo, Italy [Hamilton, 2012].

The testing of membranes is proceeding at moderate scale. It still remains to be established whether any of these membranes being tested will have the performance required for useful commercial application. Their use also depends on successful development of warm gas desulphurisation. The technology is thus assessed as being at TRL-5 presuming a favourable outcome from the current testing. The development of warm gas desulphurisation in more advanced and is assessed as being at TRL-8 presuming that the demonstration at Polk is successful.

Hydrogen separation membranes have the potential for substantial increases in efficiency and reductions in cost of power plants with pre-combustion capture and they have the potential for high CO_2 capture rates. Commercialisation of high temperature membranes must surmount challenges of:

1. Manufacturing membranes with consistently high flux properties and long lifetimes in the presence of impurities contained in coal derived fuel gas;
2. Fabrication of the membrane units themselves with gas inlet and outlet interconnects;
3. Scale-up to large unit sizes.

4.2. Sorbent –Enhanced Water Gas Shift (SEWGS)

A concept called Sorption Enhanced Reaction uses a packed bed containing a mixture of a steam methane reforming or water gas shift conversion catalyst and a selective adsorbent which removes CO_2 from the high temperature reaction zone, thus driving the reaction to completion [Hufton, 2005]. The adsorbent is periodically regenerated using PSA or TSA.

In the Sorption-Enhanced Water Gas Shift (SEWGS) process the water gas shift conversion reaction:

$CO + H_2O \rightarrow CO_2 + H_2$

is executed with multiple vessels filled with catalytically active CO_2 adsorbent, such as promoted hydrotalcite. The removal of CO_2 from the gas phase drives the equilibrium to the right hand side, maximising the production of H_2 and minimising the residual CO and the steam requirement. The hot gas from the SEWGS reactors, at about 400°C, can be fed directly to the gas turbine, thereby avoiding the energy losses associated with cooling the hydrogen gas fuel gas. The sorbent is regenerated by steam. A commercial sized plant is envisioned to consist of multiple fixed beds.

4.2.1. Performance and costs

The projected performance and costs of an IGCC SEWGS plant using the ALKASORB+ sorbent developed during the CAESAR project and comparable reference plants is given in Table 10 [Jansen, 2013].

Table 10 Cost and performance of IGCC SEWGS and reference plants

	IGCC	IGCC Selexol	IGCC SEWGS	Advantage of SEWGS vs Selexol
Net electric efficiency, % LHV basis	47.1	36.0	39.7	+3.7
CO_2 avoided, %	-	86.5	93.7	+7.2
LCOE, €/MWh	66.3	89.5	82.3	-7.2 (-8%)
CO_2 avoidance cost, €/t (IGCC base)	-	36.7	23.4	-13.3 (-36%)

The main application of SEWGS is considered to be IGCC rather than production of hydrogen for distributed use or industry, as IGCC can take full advantage of the high temperature of the hydrogen and is not penalised by its medium purity (90-95 mol%).

SEWGS is expected to also enable significant improvements in efficiency and costs of CO_2 capture in natural gas combined cycle plants [Manzolini, 2011].

Overall, SEWGS has the potential for substantial increases in efficiency and reductions in cost for pre-combustion power plants. Development issues include the performance, capacity and durability of sorbent using real power plant fuel gas and the reliability of valves.

The thermodynamic performance has been examined in some detail [Gazzini 2013] Specific energy consumptions of between 2.0 and 2.5 kJ/tonne CO_2 avoided were calculated. This equates to 0.8 to 1.0 GJ/tonne electric when the power plant is 40% efficient. Good heat integration is essential to obtain this performance and the better figure is for a sorbent with a higher capacity. The process requires recovery of latent heat from steam used in the regeneration cycle and involves expansion of CO_2/steam to subatmospheric pressure, condensation of the steam and recompression of the CO_2.

4.2.2. Current Status, technology readiness level and development requirements

SEWGS has been developed at the laboratory pilot scale (70kg CO_2/d) in the EU FP7 project CAESAR. The next stage in the process development would be pilot testing (35t CO_2/d) with coal based syngas to prove long term stability of the sorbents and reliability of key equipment [Jansen, 2013]. High temperature valves would be required for switching gas flows between the beds but availability of suitable valves is reported to not be an issue.

The system requires far deeper integration in the pre-combustion process than for typical post combustion capture technologies. Thus whilst validation of the subsystem can be done at scale moving to demonstrate the full system integrated into the IGCC plant will be more difficult. However the other equipment required for the deep integration is all based on established designs although the various expanders required will need to be custom designed for the service. The technology is assessed as TRL-5 and it should be possible to progress the development into the large scale demonstration phase without necessarily applying the deep integration needed to achieve the target high efficiency.

4.3. Low temperature separation

CO_2 can be separated from syngas by reducing the temperature resulting in liquefaction of CO_2. This is normally referred to as ‘low temperature’ separation rather than ‘cryogenic separation’ because the temperatures involved is typically around -60°C, whereas ‘cryogenic’ normally refers to temperatures below about -150°C. A disadvantage of low temperature separation is that the percentage capture of CO_2 is limited by phase equilibria. To achieve a capture rate of 90%, which is normally expected for capture processes, high pressures in excess of 10MPa are needed [Berstad, 2010]. An alternative would be to combine the phase change separation with solvent separation. An advantage of low temperature separation is that a liquid CO_2 stream can be produced, which can be pumped to high pressures thereby avoiding most of the energy consumption and cost of CO_2 compression.

The cooling required for low temperature separation can be provided by expansion of the process gas or by external refrigeration. A low temperature CO_2 capture process with an external refrigeration is shown in Figure 33.

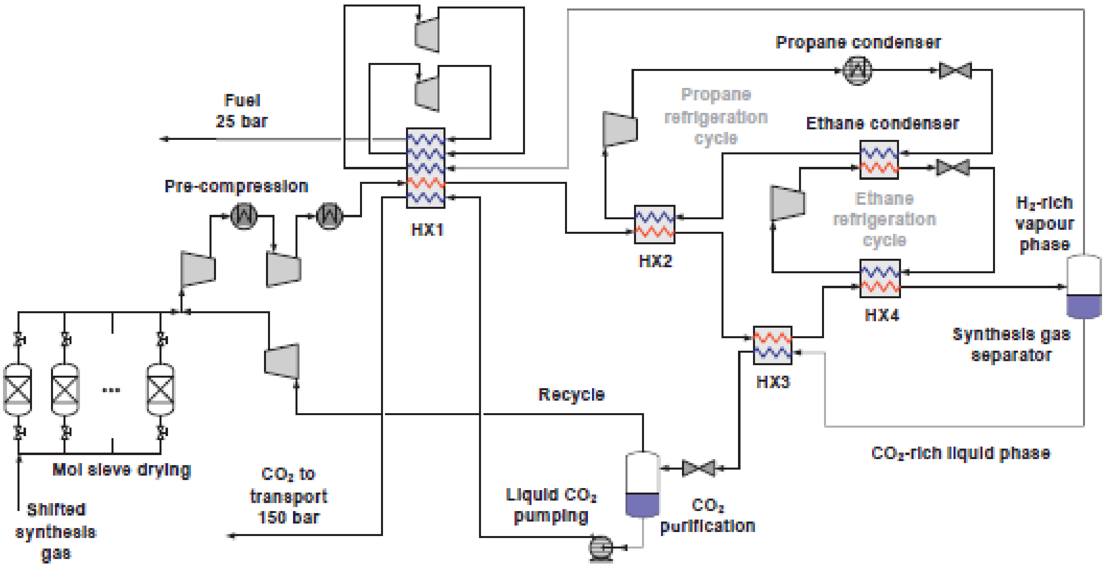


Figure 33 Low temperature CO_2 capture unit with external refrigeration [Berstad, 2012]

Autothermal phase change separation process configurations have proposed by MHI and BP [Mori, 2013]), an example of which is shown in Figure 34. The feed gas is compressed and the clean hydrogen-rich gas is expanded in a turbine (inlet pressure 6-18 MPa, outlet pressure around 3MPa).

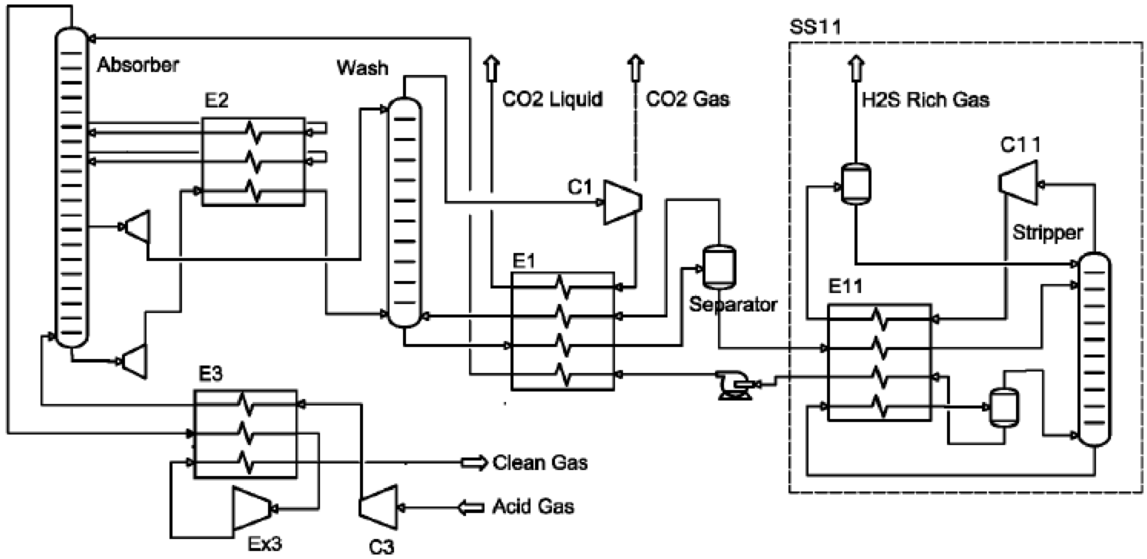
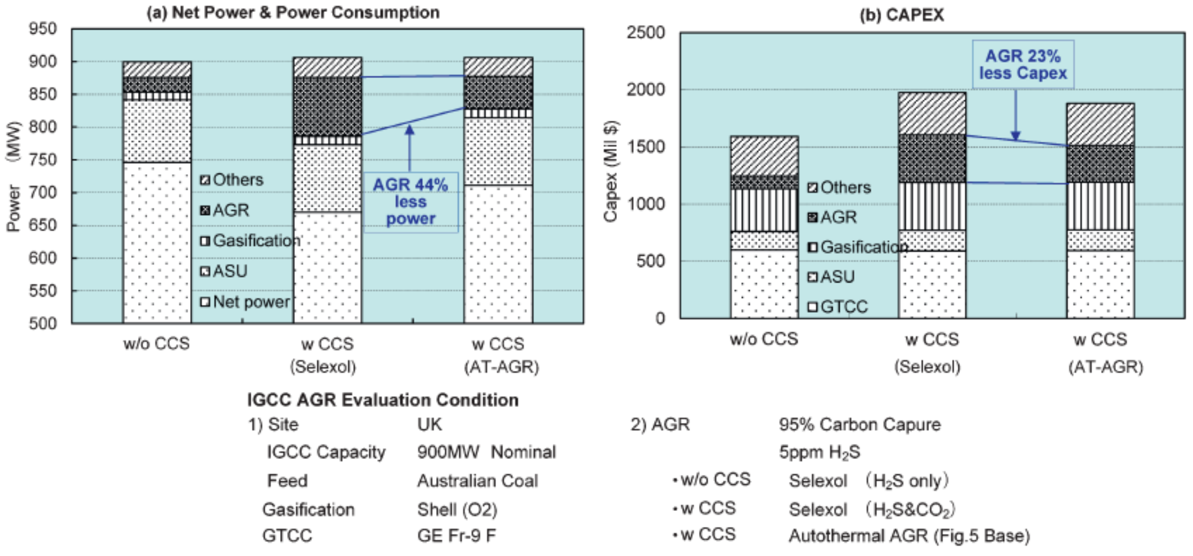


Figure 34 Autothermal CO_2-H_2S co-capture phase change separation AGR [Mori, 2013]

4.3.1. *Energy requirement / cost evaluation*

Performance and costs of autothermal acid gas removal are shown in Figure 35 [Mori, 2013]. The power consumption of the AT-AGR process is 44% less than that of Selexol and the CAPEX is 23% less.



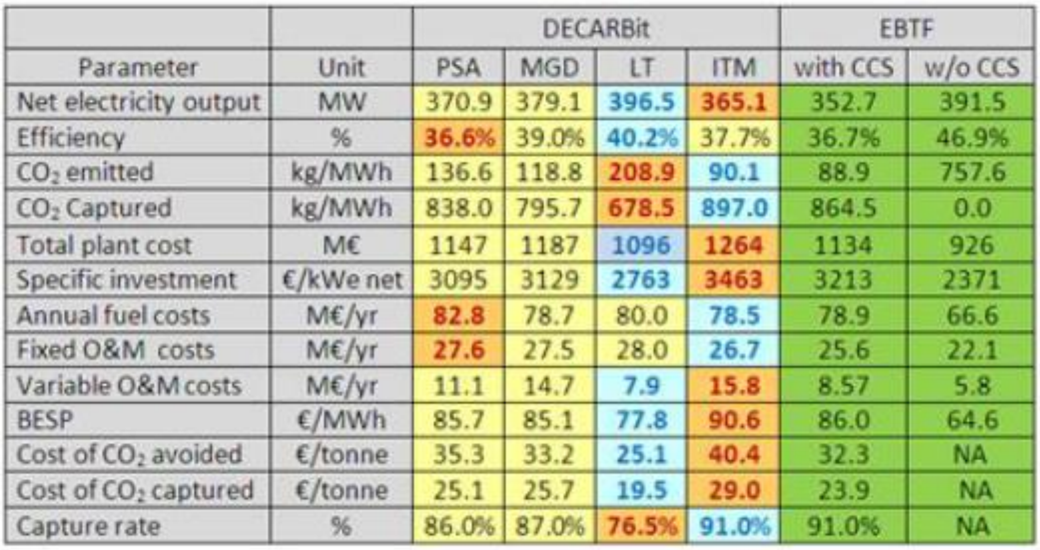
IGCC AGR Evaluation Condition

1) Site UK
IGCC Capacity 900MW Nominal
Feed Australian Coal
Gasification Shell (O2)
GTCC GE Fr-9 F

2) AGR 95% Carbon Capure
5ppm H_2S
・w/o CCS Selexol （H_2S only）
・w CCS Selexol （H_2S&CO_2）
・w CCS Autothermal AGR (Fig.5 Base)

Figure 35 Economic evaluation of IGCC with autothermal AGR [Mori, 2013]

The EU DECARBit project carried out economic assessments of pre-combustion capture using pressure swing adsorption (PSA), membrane gas desorption (MGD), low temperature separation (LT) and high temperature ion transport membrane oxygen production (ITM). The costs are shown in Figure 36, along with the European Benchmarking task force (EBT)'s costs of plants with and without Selexol CO_2 capture [DECARBit, 2012]. The costs per tonne of CO_2 avoided are broadly similar or higher for the new technologies, with the exception of low temperature separation. However, the LT separation process they considered has a relatively low capture rate of 76.5%.



		DECARBit				EBTF	
Parameter	Unit	PSA	MGD	LT	ITM	with CCS	w/o CCS
Net electricity output	MW	370.9	379.1	396.5	365.1	352.7	391.5
Efficiency	%	36.6%	39.0%	40.2%	37.7%	36.7%	46.9%
CO_2 emitted	kg/MWh	136.6	118.8	208.9	90.1	88.9	757.6
CO_2 Captured	kg/MWh	838.0	795.7	678.5	897.0	864.5	0.0
Total plant cost	M€	1147	1187	1096	1264	1134	926
Specific investment	€/kWe net	3095	3129	2763	3463	3213	2371
Annual fuel costs	M€/yr	82.8	78.7	80.0	78.5	78.9	66.6
Fixed O&M costs	M€/yr	27.6	27.5	28.0	26.7	25.6	22.1
Variable O&M costs	M€/yr	11.1	14.7	7.9	15.8	8.57	5.8
BESP	€/MWh	85.7	85.1	77.8	90.6	86.0	64.6
Cost of CO_2 avoided	€/tonne	35.3	33.2	25.1	40.4	32.3	NA
Cost of CO_2 captured	€/tonne	25.1	25.7	19.5	29.0	23.9	NA
Capture rate	%	86.0%	87.0%	76.5%	91.0%	91.0%	NA

Figure 36 The main techno-economic results obtained from DECARBit [DECARBit, 2012]

In order to compare these processes in terms of energy efficiency the figures have been used to calculate the amount of work which each process needs to perform the separation required to abate 1 tonne of CO_2. This measure is chosen as it is universally comparable to both the

theoretical work required for separation and to that of competing processes. Although thermal energy is often used when comparing some technologies, especially those based on thermal regeneration of solvent, this is not necessarily a good measure for wider comparisons.
The results in GJ/tonne avoided derived from the capture rate and efficiency reduction figures are:

• Baseline	1.17GJ/tonne
• LT	0.94GJ/tonne
• MGD	0.95GJ/tonne
• PSA	1.27GJ/tonne

4.3.2. Current Status, technology readiness level and development requirements.

Low temperature separation in general is a well-established technology, using mostly conventional equipment. Key elements have been demonstrated at laboratory and semi-industrial scale [Bouwers, 2010]. A multi-stage radial turbine-expander for low molecular weight service in the autothermal phase change process has been designed and tested [Mori, 2013].

To date the processes for low temperature separation are all at the stage of proposals for process line ups using mainly conventional refrigeration and heat exchange equipment. The arrangements for the application have thus been formulated but actual testing and demonstration has not been attempted. The technology readiness level is assessed as TRL-2 with the rider that rapid development should be possible since the processes use conventional equipment.

4.4. Low temperature separation with CO_2 recirculation – The Timmins process

An interesting variant of pure low temperature separation has been proposed by Timmins. In this process a recycle loop of the syngas is created and CO_2 levels are allowed to build up so that CO_2 can be removed as a liquid by light refrigeration. This has the advantage of greatly reducing the energy required to compress the CO_2 to export conditions. The process makes use of the capacity of the raw syngas to strip CO_2 from CO_2 loaded Selexol and thus avoids the need to supply heat for regeneration. The general arrangement is shown in Figure 37.

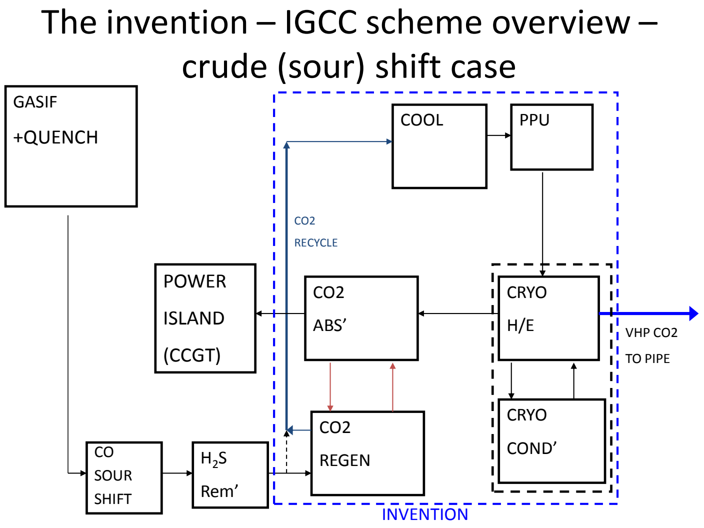


Figure 37 Overall flow scheme - Timmins low temperature CO_2 removal process

The syngas is first used to strip CO_2 from rich Selexol at a temperature of around 70°C. The CO_2 enriched syngas is then circulated through a pre-processing unit to remove water and then a refrigeration unit where part of the CO_2 is condensed and pumped away for export. The syngas with the remaining CO_2 is then contacted with the lean solvent in an absorber running at around 20°C. This temperature difference is enough to ensure that the rest of CO_2 is substantially removed from the syngas for recycling. The net effect is to create a gas loop with a high CO_2 partial pressure which facilitates the liquefaction of the net CO_2 production with light refrigeration. The inventors claim a substantial energy saving. Independent assessment has been carried out [Garrido 2012] which was largely in agreement. However it was found that careful attention has to be paid to the heat recovery network to attain the performance. Also some additional losses occur due to the solubility of CO (Carbon Monoxide) in the Selexol. This has to be flashed off at reduced pressures and recompressed into the system requiring some additional power. It is uncertain whether a change in the solvent could ameliorate this.

The shift conversion of CO to hydrogen can be placed within the recycle loop or before it. The CO solubility issue should then be eliminated. Even though the shift reaction equilibrium will be affected by the increased concentration of CO_2 in the loop the equilibrium conditions are enough to reduce CO to an acceptable level in the final hydrogen product. There will be some carry over into the combustion turbine but this small loss in capture efficiency is compensated by the fact that the losses of dissolved CO and H_2 into the CO_2 product which occur in the conventional process are eliminated.

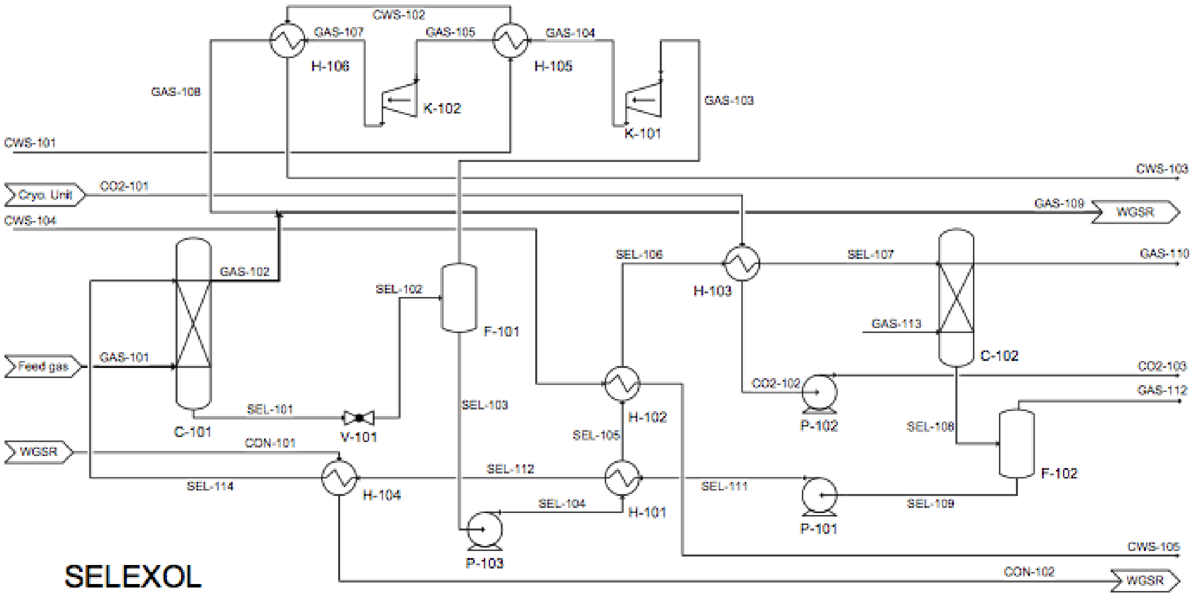


Fig 38 Arrangement of Selexol process in Timmins process

4.4.1. *Energy consumption and costs*

Estimates published by the inventors suggest up to 50% reduction on energy consumption although the detailed analysis suggests that this may be less. No detailed cost estimate has been located in the literature but as the main driver of cost is the efficiency the energy reduction is indicative of what the LCOE reduction could be.

4.4.2. Technology readiness level

The process makes use of existing technologies but to date has only been proposed as an application and no pilot or demonstration testing has been done. Thus the technology readiness level is assessed as TRL-2. However rapid development should be possible.

4.5. Fuel cells

The potential for higher efficiency power generation using fuel cells has been recognised for a long time. There is active development work on various fuel cell technologies in many companies and countries but units for large scale power generation are not yet available. Certain types of fuel cells have high energy efficiencies and they are also able to inherently capture CO_2, which means that the incremental cost of including CCS could be low. This section of the report focuses on such fuel cells.

Some other fuel cells are designed to use hydrogen, which could be produced in plants with pre-combustion capture. Hydrogen fuel cells could be attractive particularly for distributed combined heat and power production, which would make hydrogen production with pre-combustion CCS a more favoured technology if their cost and efficiency were better than those of combined cycle plants.

NETL has undertaken detailed technical and economic assessments of Integrated Coal Gasification Fuel Cell (IGFC) plants [NETL 2011a] and natural gas fuel cell plants with integrated CO_2 capture [NETL 2011b], both based on solid oxide fuel cells. These types of fuel cells are currently developed at a 60kWe scale, making them around TRL-6. A block diagram of the IGFC plants is shown in Figure 39. Desulphurised fuel gas from coal gasification is fed to the anode of the fuel cell and the anode off-gas, consisting mainly of CO_2 and H_2O, along with small amounts of CO, H_2 and inerts is fed to an oxy-fuel combustor, and the resulting CO_2 is compressed for storage. Pre-heated air is fed to the fuel cell cathode and air with a reduced oxygen content from the cathode is cooled in the pre-heater heat exchanger. The fuel cell operates at a temperature of 650-750°C and a pressure either close to atmospheric or at 2MPa.

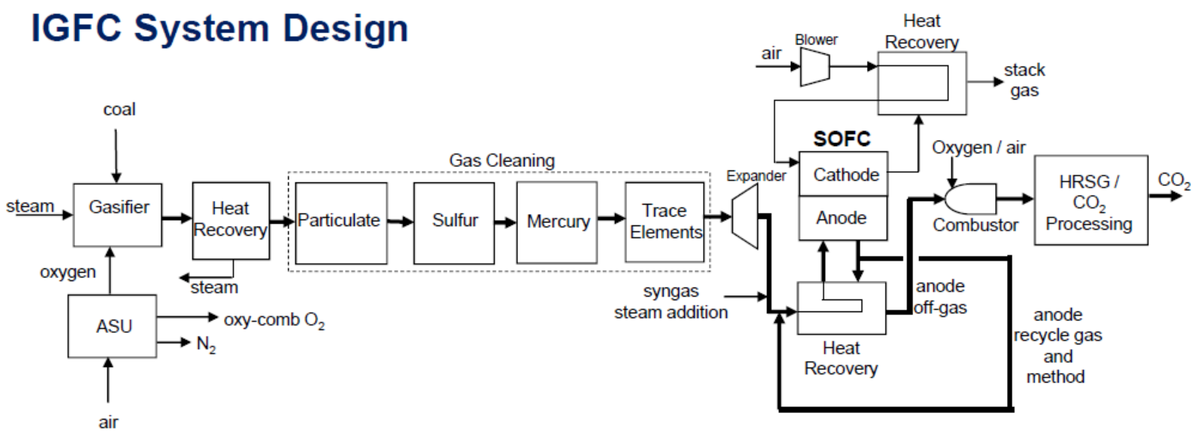


Figure 39 Integrated Gasification Fuel Cell (IGFC) plant [NETL 2011a]

The study assesses plants based on two types of coal gasifier; a conventional Conoco Phillips E-Gas gasifier and a catalytic fluid bed gasifier, which is at an early stage of development. The E-Gas gasifier produces a gas with a relatively low methane concentration and the catalytic gasifier produces a gas with a much higher methane concentration (around 30%), which is an advantage for an IGFC plant. Conventional gas cleaning technologies, including Selexol desulphurisation, are assumed to be used up-stream of the fuel cells. Warm gas cleaning technologies may result in further efficiency and cost improvements. The plants have CO_2 capture rates >98%.

NETL has also published a techno-economic assessment of natural gas fuel cell power plants with CO_2 capture. These plants are similar to the IGFC plants except that natural gas autothermal reforming replaces coal gasification and gas cleaning.

4.5.1. Performance and costs

The power generation efficiencies and Levelised Costs of Electricity of fuel cell plants and the improvements compared to reference IGCC and natural gas combined cycle plant with post combustion capture reported in NETL's reports are shown in Table 11. The data are given for reference plants based on conventional solvent scrubbing and gas turbine combined cycles, baseline fuel cell plants and plants with various improvements leading to the best efficiencies and costs. Details of these improvements and their individual contributions to the cost reductions are given in the references. Note the efficiencies are on an HHV basis, unlike most NGCC efficiencies which are on an LHV basis. LHV efficiencies are around 10% (not percentage points) higher for natural gas power plants.

Table 11 Efficiencies and costs of fuel cell power plants with CO_2 capture.

		Efficiency		LCOE	
		%, HHV	Difference % point	$/MWh	Difference %
E-Gas gasifier	Reference IGCC	31.0	-	110.4	-
	Baseline fuel cell	40.0	+9.0	96.3	-12.8
	Improved fuel cell	46.5	+15.5	72.5	-34.3
Catalytic gasifier	Baseline fuel cell	50.5	+19.5	79.8	-27.7
	Improved fuel cell	60.0	+29.0	61.2	-44.6
Natural gas	Reference NGCC	42.8	-	85.9	-
	Baseline fuel cell	53.3	+10.5	85.0	-1.0
	Improved fuel cell	65.9	+23.1	63.1	-26.5

The assessment of IGFC plants was undertaken on a consistent basis to NETL's 2007 baseline plants study, in which an IGCC plant with CCS based on the E-Gas gasifier had an HHV efficiency of 40% and a LCOE of $105.7/MWh and a supercritical pulverised coal plant with post combustion capture had an efficiency of 27.2% and an LCOE of $114.8/MWh. The baseline IGFC plant based on E-Gas gasification has an efficiency of 40%, i.e. 8.3 percentage points higher than an IGCC plant and 12.8% points higher than the plant with post combustion capture. The efficiency of the plant based on catalytic gasification, pressurised fuel cells and the most favourable sensitivity assumptions is 60%. The LCOE of the baseline IGFC plant is $96.3/MWh, i.e. a 9% reduction compared to the IGCC plant and the most favourable IGFC plant has a LCOE of $61.2/MWh, i.e. a 42% reduction. This analysis indicated that IGFC has the potential for large improvements in efficiency and LCOE.

The additional costs are dominated by the SOFC power island and also the small ASU. Because the SOFC power island replaces the conventional gas turbine in an IGCC plant it is questionable as to what portion of its costs should be attributed to CO_2 Capture. One approach could be to compare with the costs of the conventional power island but as many other aspects of the plant also change this would only give a rough indication. The full costs of the ASU are however attributed to the capture process. The NETL study was a pathway study for development of a SOFC based capture system and did not include a baseline IGFC plant without capture. Much of the development of IGFC should be considered as being in the domain of mainstream power generation technology.

4.5.2. Thermodynamic considerations

A key element of the efficiency improvements is the superior electrical conversion performance of the solid oxide fuel cell. In order to capture CO_2 a version of the SOFC in which the anode and cathode gases are kept separate is required. The SOFC electrolyte membrane is an oxygen conductor and it is this property which is the essence of its ability to capture CO_2 since it performs the processes of combustion and oxygen separation in a single device. The pathway study by NETL considers improvements to the current performance of SOFC's which enhance its conversion efficiency. The main one is to reduce the cell overpotential from 140mv to 70mv. As the cell potential is only around 1000mv this projected 70mv reduction represents a significant efficiency gain. The second is to pressurise the cells which raises the Nernst potential. However their studies indicated that it is so costly to build the necessary pressure containments that there is no economic advantage.

The methane content of the fuel to the SOFC affects the overall efficiency. This is because methane reforming in the cell assists with the cooling which otherwise has to be provided by increased cathode air flow. The internal transfer of heat from the reforming reaction is thermodynamically more efficient than providing external cooling. Hence the development of a catalytic gasifier which produces higher methane content syngas is an important development. Blending natural gas into the syngas has a similar effect and could be considered if gas prices are favourable.

The only change to fuel cell design required to allow CO_2 capture is that the anode and cathode gases have to be kept separate. The first designs of cell allow the cathode and anode gases to combine which is far simpler to manifold and results in complete combustion of the fuel. In the capture design the final combustion is accomplished by mixing with pure oxygen so a small ASU is required.

4.5.3. Technology readiness level

Although SOFC stacks have been developed to substantial size the full integration of these into an IGCC with the capture feature has not yet been tested. Thus only some of the subsystems could be claimed as fully validated. Furthermore the degradation of the SOFC stacks which slowly reduces the voltage and hence efficiency over several thousand hours has to be improved. In addition the better performance offered by catalysed gasification requires further development of this technology. The technology readiness level is thus assessed at between TRL-4 and TRL-6, the lower level because there has yet to be validation of low enough SOFC stack degradation to take the concept to commercialisation.

5. Oxy-Combustion

5.1. Oxy-combustion for solid fuel fired boilers

Oxyfuel combustion for power generation with CO_2 capture is the use of oxygen and recycling part of the flue gas instead of air as oxidant to the fuel. This results in a flue gas with a high concentration of CO_2 and H_2O which would require physical separation to deliver the specified purity of CO_2 for transport and storage.

Generally, technology development involves the following areas:

- Fuel preparation (particularly important to brown coal application)
- Boiler design and operation
- Oxygen production
- Flue gas processing
- CO_2 processing unit (CO_2 Purification Unit/Gas Processing Unit)

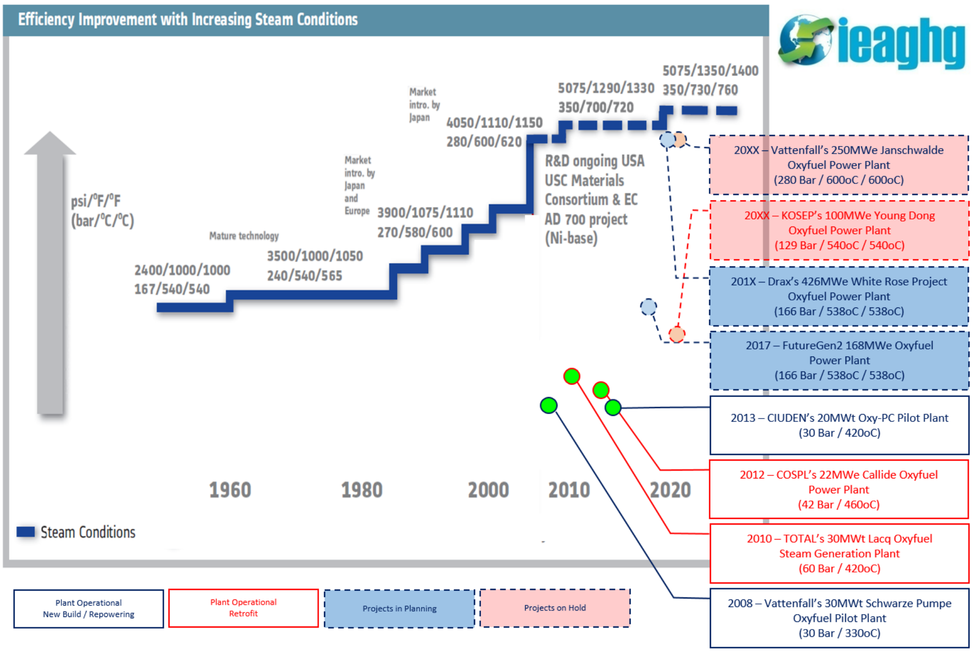
Currently, technologies for oxyfuel combustion for PF or CFB coal fired power plants have reached the necessary maturity ready for large scale demonstration (i.e. 100 – 400 MWe). This is a crucial step to bring this technology forward and achieve the goal of commercialisation by a 2020-2030 horizon. The large scale demonstration is an important step to sustain the current R&D investment and activities necessary to develop technologies and key components that would lead to cost reduction and improve efficiencies.

Boiler Design and Operation

Technology development for oxyfuel combustion boilers will broadly follow the development of conventional air fired boilers as shown in Figure 40.

The following key areas could be the main focus of future development for oxyfuel combustion PC and CFB boilers:

- Co-firing of biomass or other alternative fuels (petcoke, etc.).
- Development of CFD modelling tools for heat transfer, combustion characterisation, emissions, etc.
- Materials development contributing to the understanding of the impact on the boiler materials, welding, etc. when operating under oxyfuel combustion condition.
- Enabling the use of warm recycled flue gas to increase efficiency (i.e. materials development along the flue gas recycle path).
- Development of low flue gas recycle rate and high oxygen content in the furnace – for CFB only.
- Power plant flexibility.



S. Santos (16/04/2014) - figure of steam conditions adapted from Alstom's paper

Figure 40 – Development pathway of PF coal fired boiler – also depicting the current status of oxyfuel combustion boiler development
Figure adapted from [Marion et al (2009]

It has been established that the basic principles used in designing conventional coal fired boilers and burners are also applicable to design of oxy-fuel combustion boilers. Development of oxyfuel combustion boilers will be evolutionary in nature rather than through emergence of new breakthrough technologies.

For the demonstration and first generation Oxyfuel Combustion Power Plant (PC or CFB) applied to coal or other solid fuels, the main consideration is the combustion characteristics of the fuel and the optimization of design and operation associated with that fuel. In the early deployment of this technology, it is expected that conservative designs based on known boiler tube materials currently used by their air fired counterpart will be used. Operation of the boiler (i.e. heat extraction rate) will be adjusted according to the dew point temperature of the resulting flue gas. Current development will focus on flue gas processing (of the recycled flue gas) to remove SOx, NOx, halogenated compounds, and water to reduce the risk of material failures due to corrosion. These are vendors' specific technology development. It is expected that future generation oxyfuel boilers will follow the development of advanced ultra-supercritical PC fired boilers to higher temperatures and pressure (i.e. 300 bar / 700°C).

5.2. Pressurized Oxy-combustion

Operating the combustion boiler under pressure is claimed to offer some advantages over atmospheric operation. EPRI and US DOE are supporting developments of this technology. Also ITEA, Italy, have described a flameless pressurized oxycombustion variant. A further variant is a staged pressurized oxycombustion (SPOC).

5.2.1. *Staged Pressurized Oxycombustion (SPOC)*

This technology applies two refinements to the atmospheric oxycombustion process. The first is to operate the combustion boiler under pressure. The reasons for this are to avoid the need for compression of the CO_2 rich flue gas, reduce the energy used for CO_2 recycle and to enable recovery of some the latent heat in the steam component of the flue gas. The second refinement is to apply staged combustion which eliminates the need for recycle CO_2 to moderate the temperatures in the combustion chamber. This is done by staging the addition of fuel so that in the first combustion chamber/boiler there is a sufficient excess of oxygen to limit flame temperature. Typically 4 combustor/boilers would be used in series operating under pressure. These technologies are supported by the US DOE and EPRI. Washington University in St. Louis (WUSTL) is working on the evaluation of the technology. The SPOC process is described in Gopan 2014. The arrangement is shown in figure 41.

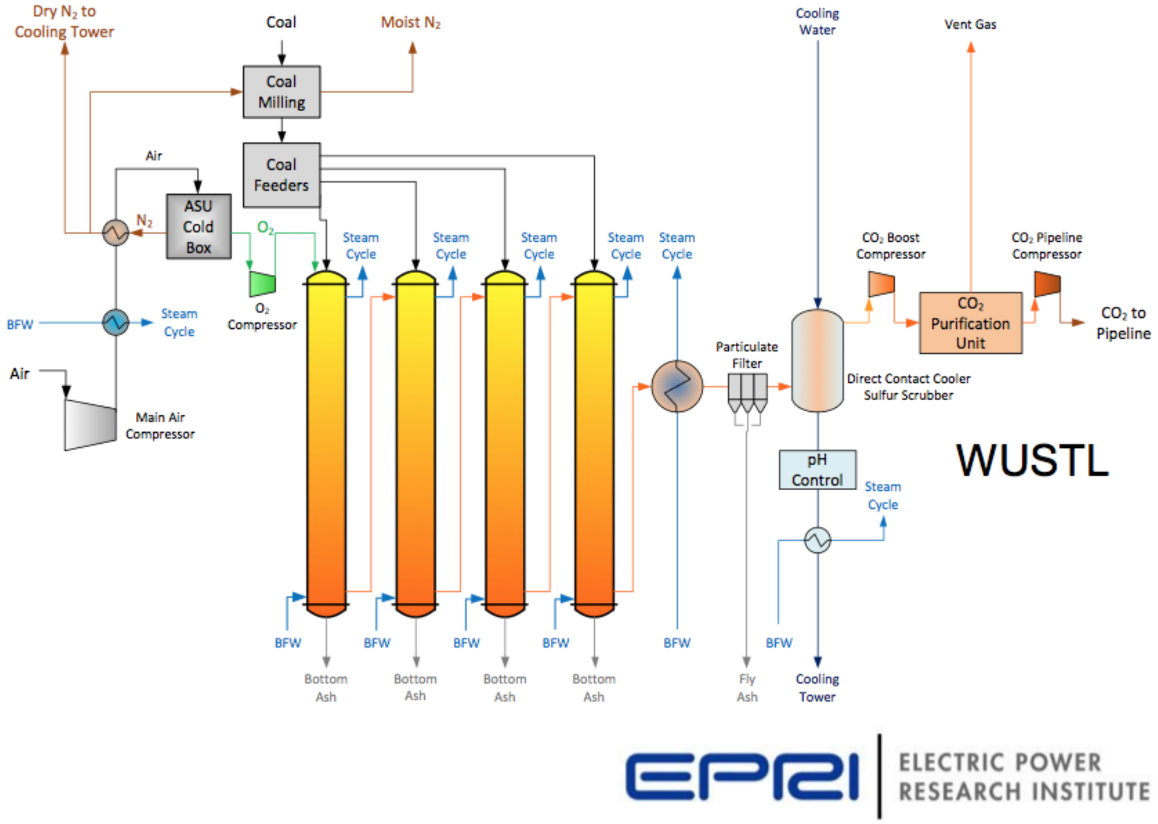


Figure 41 Staged pressurized oxycombustion flow scheme

5.2.2. *Conventional and Flameless Pressurized Oxy-combustion (FPOC)*

Pressurized oxycombustion trades extra power required to compress oxygen into the combustion chamber against reductions in CO_2 compression power, power for recirculating flue gas and recovery of latent heat from condensation of steam in the raw flue gases which occurs at a useful temperature for power recovery because of the higher condensation temperatures. It is claimed that overall efficiency is thus improved. The figure from a recent presentation by EPRI on novel CCS cycles illustrates the basic process and proposes that combustion takes place in a bubbling bed. Aerojet Rocketdyne is involved with the development and Figure 42 illustrates this conventional pressurized concept.

An interesting variant, Malavasi 2014, is to carry out the pressurised combustion under flameless conditions. This has been tested at a scale of 5MWt at ITEA, a small combustion R&D company within the Italian Sofinter-AnsaldoCaldaie-Macchi Group, in Italy. Claimed overall efficiency is 33.4% (LHV basis). The basic scheme is shown in figure 43. By using a hot recycle the entire combustion chamber is kept at a uniform high temperature of around 1700K. It is claimed that slag melts and forms into large droplets which can be removed from the bottom of the combustor after water quench as vitrified pearls of non-leachable material.

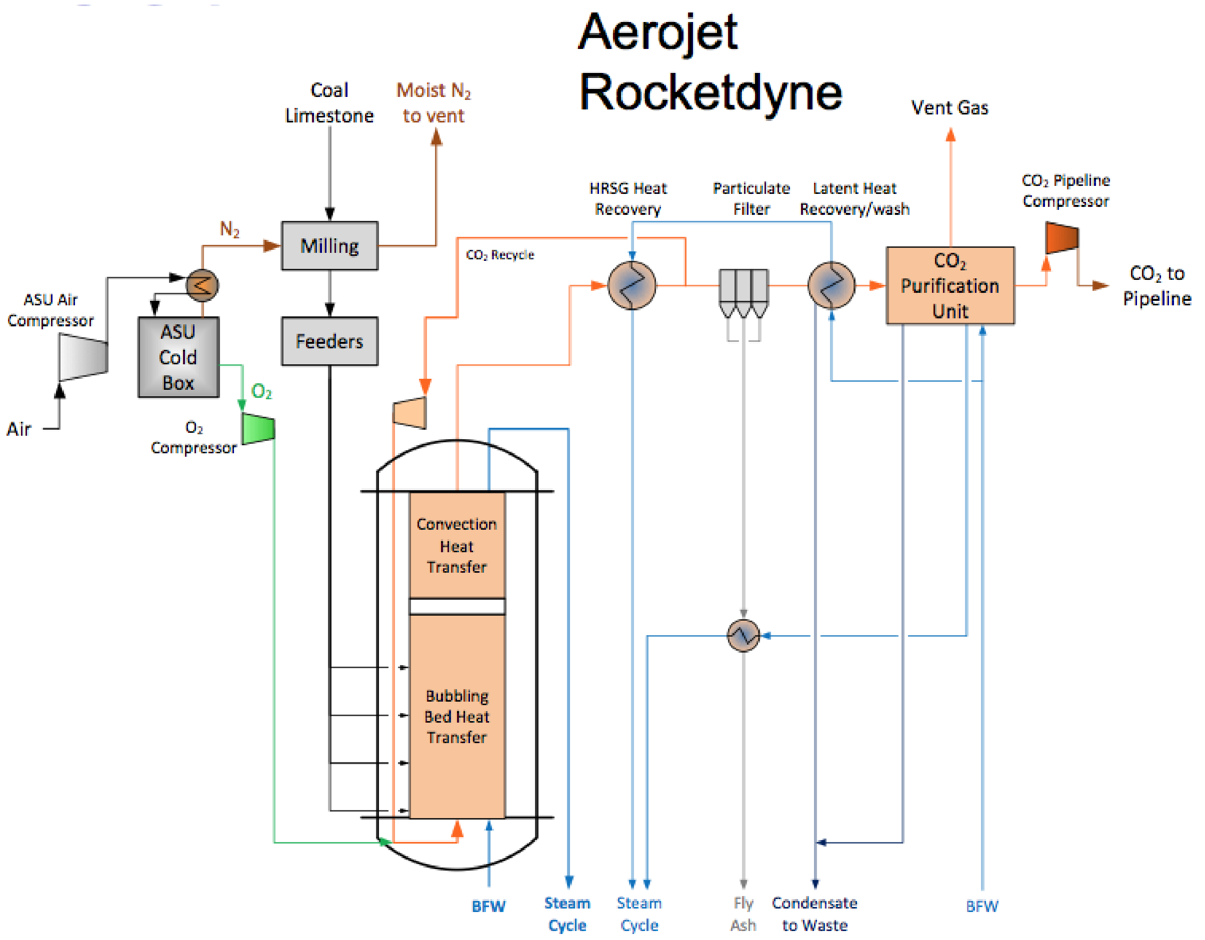


Figure 42 Flowscheme of pressurized oxycombustion

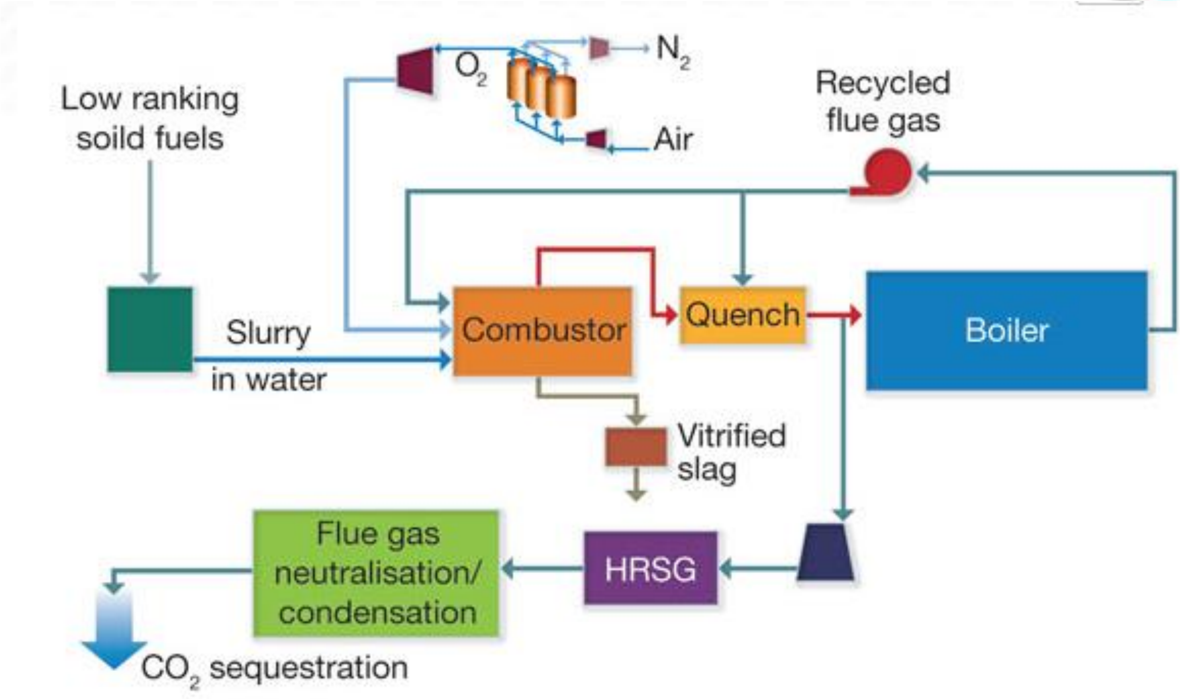


Figure 43 Flow scheme of flameless oxycombustion

5.3. Oxygen Production

5.3.1. Cryogenic Air Separation

The major cost of CO_2 capture by oxy-combustion is due to the energy consumption and capital cost of the air separation unit (ASU). Cryogenic air separation is considered one of the mature technologies within the CO_2 capture chain. It would be difficult to achieve any major improvement to the efficiency of conventional ASUs. However, ASUs for oxyfuel combustion applications that deliver oxygen with low purity (i.e. 95 – 97% O_2) and low pressure (i.e. 1.2 to 1.8 Bara) have opened up opportunities for step change improvement in energy efficiency [Beysel, 2009; Higginbotham, 2011; Shah, 2011(a); Higginbotham et al, 2011; Goloubev, 2012]. It is expected that advanced ASU cycles using three columns or dual reboilers will be central to the ASU development pathway for oxyfuel combustion applications. Based on these cycles, it is claimed that about 5 – 35% efficiency improvement could be achieved as compared to the conventional two column ASU cycle.

Key to the development of the air separation unit is the demonstration of a large scale single train ASU (i.e. in the range of 5,000 to 10,000 t/d O_2). Today, the largest operating ASU is 3,900 t/d O_2. A contract has recently been awarded to build the largest single train ASU at 5,250 t/d O_2 in India for gasification application. This is expected to be operational by 2015. This kind of commercial deployment will naturally feed into the development of large scale single train ASUs for oxyfuel combustion application which should help reduce capital and operating costs.

The following key areas could be the main focus of future development of cryogenic ASU for oxyfuel combustion application [Golubev, 2012]:

- Development of advanced ASU cycles for oxyfuel combustion applications and meeting the flexible operation requirements of the power plant.

- Development of the main air compressor to provide wider range of turn down.
- Development of process control systems to allow smooth operation of the ASU meeting the variable O_2 demand of the power plant.
- Development of process integration options of the ASU with the power plant and the CPU.
- Enabling the cryogenic ASU as energy storage platform. This development will be driven by the peak electricity price and requirements for power plant flexibility.
- Utilisation of waste N_2 from the ASU (i.e. use of additional Brayton Cycle using N_2 as working fluid).

Additionally, it expected that the cryogenic ASU will gain several incremental improvements in the future once the large scale demonstration plants are initiated. It should be noted that the selection of an appropriate ASU cycle to meet the requirements of the power plant is an important aspect to the delivery of an optimized CAPEX and OPEX air separation unit for oxyfuel combustion application.

Some of the key areas of development where improvements to the ASU could be gained and capital cost could be reduced include the following:

- Improvement to the Front End Purification Processes (i.e. packing selection for Direct Contact After Cooler, that could reduce pressure drop and minimize vessel diameter).
- Improvement to the main heat exchanger (i.e. use of brazed aluminium heat exchanger with larger core sizes and lower pressure drop).
- Improvement of the distillation column (i.e. use of high capacity structured packing that will lead to low pressure drop and smaller diameter).
- Improvement to the reboiler design (i.e. use of improved Thermosyphon reboiler design).

5.3.2. Other Novel Oxygen Production Technologies

Inexpensive, large scale oxygen production is crucial to the development of the next generation of integrated power plants with CCS based on oxyfuel coal combustion or IGCC technologies. Currently, there are other oxygen production processes being developed that could have the potential to deliver improvements. Some of the leading technologies include:

- Ion transport membrane (ITM)
- Oxygen transport membrane (OTM)
- Ceramic Auto-thermal Recovery System (CARS)

Figure 44 present the status of development and the maturity levels of the different oxygen production processes.

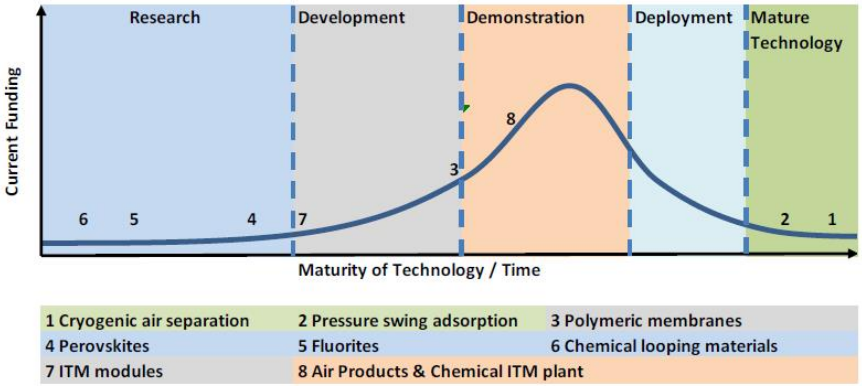


Figure 44 – Maturity and total R&D investment of different oxygen production processes [De Costa et al, 2013]

In general, the challenges to these novel oxygen production processes are to be able to scale up to the same production capacity per train and achieve the same level of reliability as compared to the current fleet of cryogenic ASUs. Basically, these technologies are also applicable to future IGCC development (i.e. not limited to oxyfuel combustion). In fact, the current trend of development indicated that early deployment will be toward IGCC rather than oxyfuel combustion applications.

The most prominent among these technologies is the development of the Ion Transport Membrane (ITM) developed by Air Products as this has already achieved small scale pilot plant operation producing ~150 t/d O_2. The basic principle of ITM is based on separation of oxygen from ionized gas using a mixed conducting dense ceramic/polymeric membrane in wafers configuration. The membranes are assembled in stacks of wafers with a central oxygen collector tube which conducts the permeate stream. This design reduces the sealing area per membrane area, whilst also providing a large membrane packing density, which translates to high oxygen fluxes per unit volume.

The ITM system is not a direct replacement for the cryogenic oxygen plant as it requires a feed of hot oxygen containing gas (i.e. air). Hence the ITM is integrated with a gas turbine so that part of the power from an ITM based oxycombustion power plant would come from this turbine. The arrangement is shown in Figure 45 [Qintrell, 2012].

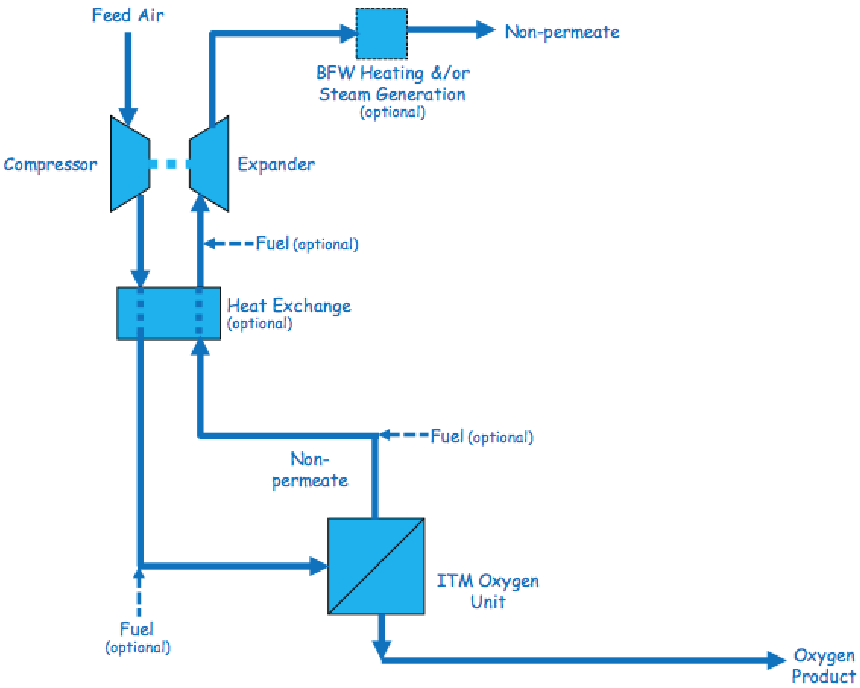


Figure 45 Arrangement of ITM oxygen process (after Quintell)

Examples of this balance between the ITM unit and the main PC power plant show that just over 30% of the gross power comes from the ITM power unit. A reduction in LCOE of 24% is claimed on the basis of process studies.

Because of the need to integrate with a gas turbine the ITM may be a better fit with pre-combustion technology where it could supply the oxygen requirements for the IGCC. The hot air supply would be derived from the main gas turbine of the IGCC. An example of this arrangement is shown in Figure 46

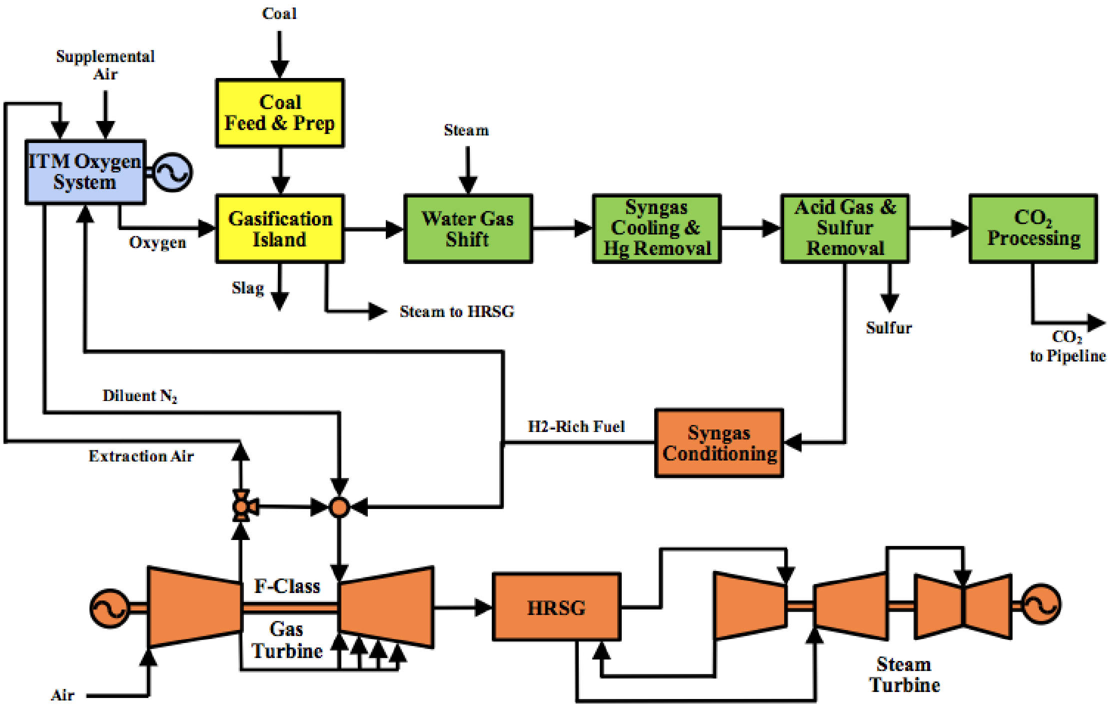


Figure 46 IGCC process with carbon capture using ITM

The Oxygen Transport Membrane (OTM) is being developed by Praxair. Primarily, the development is more focused on a system where natural gas is used as fuel or coal is gasified and the syngas is used as fuel. This involves the combination of POX and an oxy-gas boiler. The OTM is based on ceramic tubes (primarily using Peroskovites) to separate the oxygen from air. The oxygen is then delivered to the process fluid.

The Ceramic Auto-thermal Recovery System (CARS) is developed by BOC/Linde. The oxygen is separated from an air stream using a perovskite ceramic oxide adsorbent (composed of lanthanum, strontium, cobalt, and iron) at high temperature (800-900°C) in cyclical operation consisting of a two bed configuration (i.e. one bed adsorbing the oxygen and the other bed desorbing). The perovskite sorbent is alternately exposed to feed air and regeneration gas flows. Partial pressure swing (using a sweep gas) enables production of an O_2-enriched stream. Internal regenerative heat transfer is used to maintain temperature (the perovskite zone in each bed is sandwiched between two zones of heat transfer material).

5.3.3. *Thermodynamic considerations*

The work of separating oxygen from air is the main source of loss in oxycombustion processes as compared to that for separation of CO_2 from flue-gas in post combustion. The theoretical energy of separation for post combustion is about 0.15GJ/tonne. To separate oxygen from air to 95% purity requires about 0.175GJ/tonne oxygen. If burning coal with a C:H mass ratio of say 16 and excess air of say 20% the equivalent separation energy is about 0.16GJ per tonne CO_2, thus essentially the same. Note however that if natural gas is being burned (with excess air of say 5%) then oxygen has to be provided for all of the hydrogen and the theoretical energy rises to about 0.27GJ/tonne CO_2 putting oxycombustion at some considerable disadvantage for natural gas applications.

In practice efficiencies of separation are far lower than the theoretical. Typical energy consumption quoted by one leading supplier of ASU's is about 0.88GJ/tonne with the promise of reductions to as low as 0.63 GJ/tonne. Further improvements to a target of around 0.5GJ/tonne are to be expected. The figure used in NETL 2008 cost estimates was 0.84GJ/tonne (235kWh/tonne). This study used ISO conditions and it should be noted that ASU energy consumption will be affected by the actual ambient air conditions at site as these affect the power required by the main air compressor which accounts for most of the electrical load.

The conventional ASU process produces relatively pure nitrogen as a by-product although theoretically this is not needed for the oxy-combustion process. The energy for extraction of oxygen from air is about 25% lower. A membrane process with the retentate side openly exposed to air could conceivably produce only purified oxygen but no nitrogen but would be difficult to engineer. To date no process additions for oxycombustion to exploit the work put into purifying the nitrogen appear to have been identified.

Finally there are minor separation efficiency trade-offs related to the purity of oxygen which is produced. Producing a lower purity oxygen will reduce energy requirements in the ASU but savings there have to be counterbalanced by the increased energy then required for final purification of the CO_2. The purity commonly used in designs is about 95% Oxygen.

5.3.4. Costs and energy consumption

The ASU contributes to a substantial part of the cost of the capture using oxycombustion. As mentioned earlier both the capital cost and the additional energy consumption are significant. The energy consumption incurs not only fuel costs but also the capital cost of providing additional power generation. NETL produced detailed cost estimates for oxycombustion [NETL 2008]. The specific energy consumption per tonne captured calculated from their figures, both typical and advanced steam conditions, suggest a specific energy consumption of about 1.23GJ/tonne.

Examination of these estimates for oxy-combustion processes shows that the capital for a plant of equal net output increases by almost 70%. Of this increase just over 40% is for the ASU about 20% for the CO_2 clean up and compression and just under 40% for capacity increases in the main plant associated with the extra electrical load. Examination of the load increases reveals that that 65% is attributable to the ASU and 35% to the CO_2 processing unit. The capacity increases for the parasitic load are all attributable to these two elements and this approximate 1/3:2/3 ratio defines the relative importance of these two elements in driving the LCOE increase.

About 75% of the LCOE increase is due to increased capital charge and as increased capital is a large driver of the fixed and variable costs as well this probably approaches 80%. The rest of the increase is driven by the increased auxiliary power and its effect on fuel and consumables costs. Reductions in power consumption of the ASU have some knock on effect on the size of the rest of the equipment which would reduce their costs, however because of the relatively high capital element ASU energy efficiency gains would need to be carefully counterbalanced against any ASU capital cost increases.

An example has been calculated by prorating costs for improving the ASU specific power from the 0.84 GJ/tonne of the estimate to the target of 0.5 GJ/tonne a 40% reduction. Keeping ASU capital cost per tonne O_2 the same reduces the LCOE increase by 22%.

5.3.5. Technology readiness level

Oxycombustion has been successfully demonstrated at significant scale of 90MWt and the overall process can thus be assessed as being at TRL-7. Cryogenic ASU's are in general commercial service and are thus at TRL-9. However, the required capacities for a single train ASU needed to meet the oxygen demand for full scale coal fired power plant is about 5000 – 10000 tonne/day O_2 per train in order to reduce cost by achieving the economy of scale. Currently, the maximum size of plants is being increased steadily in response to demands primarily in the other industries (i.e. IGCC, coal gasification, gas to liquid, coal to liquid, steel, etc…). Five trains of 5250 t/day O_2 is currently under construction supplied by Linde for Reliance Industry. Furthermore, single train ASUs with capacity of 7000-8000 t/day O_2 per train are now being quoted by OEMs.

Of the new oxygen production processes the ITM is the most advanced as this has been tested at a scale of 150t/day. Plans are in place to develop a 2000t/day unit which is of sufficient size to be regarded as commercial scale demonstration. This element is thus assessed as at TRL-7

The development of OTM is less advanced and appear to be focussed still on development of the membrane materials and stacks. The CARS system is at a similar stage of development using a small 0.7t/day pilot to test and validate the process. Both are thus assessed as being at TRL-4

5.4. CO_2 Processing Unit

The CO_2 Processing Unit (CPU) is the purification step of the CO_2 rich flue gas before its delivery to the storage site.

The CPU and its development could be sub-divided into the three key areas namely:

- Pre-treatment of the CO_2 rich flue gas from the oxyfuel boiler (i.e. removal of SOx, NOx, particulates, Hg and water)
- Inert removal via a cryogenic process and the use of an auto-refrigeration cycle using impure CO_2 as refrigerant
- Development of the process for additional recovery of CO_2 from the CPU vent.

5.4.1. Pre-treatment of the CO_2 Rich Flue Gas

The pre-treatment of the CO_2 rich flue gas is also called the "Warm Part" of the CPU. This generally involves the following processes:

- Removal of water
- Removal of SOx and NOx
- Removal of dust particulates and
- Removal of trace elements (i.e. Hg)

There are several technology vendors providing different solutions in the pre-treatment of the CO_2 rich flue gas from the boiler. It is expected that water will be removed down to <10ppm level due to the requirements of the cryogenic process downstream. The remaining NOx and SOx in the flue gas will mostly be removed prior to its entry into the "Cold Part" of the CPU. Particulates will be removed to less than 10 μg/Nm^3 level to reduce the impact to the downstream processes (i.e. erosion of heat exchangers, etc.). Mercury is considered an operational issue due to the corrosive effect to any aluminium equipment downstream. This will be removed to undetectable level similar to the standards used by the natural gas processing industry.

Within the “Warm Part” of the CPU, the technology development involving the removal of the NOx and SOx is considered an emerging technology where several vendors have presented different options.

The paper published by Air Products [White, 2008; 2011] recognising the reaction of NOx and SOx in the presence of oxygen and water producing sulphuric acids and nitric acids during compression (i.e. classic lead chamber reaction) is an important development of the previous decade that led to the development of a wide variety of processes to remove these acidic components.
Depending on the technology vendors, the design of the NOx and SOx removal unit is also dependent on the design of the Flue Gas Processing Unit (i.e. Flue Gas Desulphurisation and Flue Gas Condenser) of the Oxyfuel Combustion Technology.

Some of these options are summarised below:

- Air Products [White, 2008, 2011; White et al, 2013] proposes the use of the Sour Compression Process (based on lead chamber reaction) to knock out 99% of the SOx as H_2SO_4 and remove at least 95% of NOx as HNO_3 and HNO_2 during the compression of the CO_2 rich flue gas.

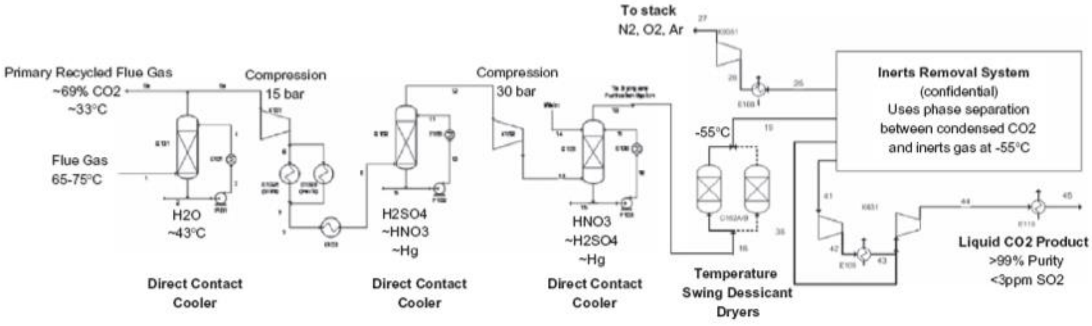


Figure 6: Air Products ''Sour Gas Compression'' technology (White et al. 2009; Murciano et al. 2011)

Figure 47 Air products sour gas compression technology

- Linde [Ritter, 2009, 2011(a), 2011(b)] proposes the use of the LICONOX process whereby 99% of the SOx is initially removed at the FGD and/or FGC. The cleaned gas is compressed to 15 Bar_a to convert NO to NO_2; and then NO_2 is removed using alkali wash (based on NH_3 water or NaOH). This would result in a removal of at least 95% of NOx as spent salt of nitrite and nitrate. An option to reduce the salt loading is possible by preheating the salt solution to 60°C therefore reducing the spent salt of nitrite to N_2 and H_2O.

- Praxair [Shah, 2011(b)] presented two possible options for pre-treatment of the flue gas. The first option uses sulphuric acid wash to recover nitric acid. This would result in a clean gas containing 50-100 ppm SOx and less than 50 ppm NOx. The second option uses activated carbon to adsorb any SOx and NOx resulting in dilute acid during regeneration.

- Air Liquide [Lockwood et. al., 2013; Lelerc et al, 2013] proposes the use of $NaCO_3$ to quench and scrub the flue gas to reduce the SOx down to less than 10 ppm, and the removal of the NOx at the knockout drum of the compressor and final removal at a separate distillation column of the cold box. Co-capture of the remaining NO_2 is also a possibility.

Among the four options presented above, only the process of Air Liquide has been tested in a large scale pilot plant (i.e. ~10 – 165 t/d CO_2 at CIUDEN's facility). Others have been tested only at smaller scale pilot facilities (i.e. < 10 t/d CO_2).

Future work in this area will primarily focus on the area of scaling up, process intensification and process integration.

5.4.1.1. Technology Readiness level

The warm gas clean up processes have only been tested at small scale. They are however based on well established technologies. Linde and Air Liquide use conservative approaches and are assessed at technology readiness level TRL-7. The Air Products and Praxair processes need validation of the flue gas compression with high SOx and NOx loading and are assessed as being at technology readiness level TRL-6.

5.4.2. Inert Removal Process

The cold part of the CPU primarily functions as the separation of the other non-condensable CO_2 components mainly consisting of O_2, N_2 and Ar. This part of the CPU technology is an evolutionary development of the liquefaction plant used in the current fleet of industrial and food grade CO_2 production. The newer innovation of this technology is the use of the auto-refrigeration cycle using impure CO_2 as refrigerant.

The CPU could consist of a cycle having a partial condensation and/or with a distillation column. The primary driver in the design of the cycle is dependent on the limits on the oxygen content of the CO_2.

Future development in this area would only require engineering data of impure CO_2 to validate refrigeration performance of the current cycle presented by various OEMs for the oxyfuel combustion applications. Development in process control systems will also get the larger R&D investment share in the future to address the power plant flexibility requirements.

Newer technologies would focus on improving the refrigeration cycle and could also include other possible refrigerants other than the impure CO_2. It should be noted that best practices developed in technologies used by the LNG industry could also be adapted to this process.

Linde has investigated [Alekzeev 2013] a range of configurations for the cryogenic part of the CPU. Specific energy requirements were found to lie in the range 0.32 – 0.42GJ/tonne CO_2 recovered for processes using either two flashes or a flash and a column. No obvious optimum process was identified and the best fit process is considered to depend on the recovery and purity specifications.

5.4.2.1. *Technology Readiness level*

All of the technologies needed to perform the cold processing of CO_2 are based on commercially available processes. The technology readiness level is assessed as TRL-8.

5.4.3. *Capture of Additional CO_2 from CPU Vent*

The capture of CO_2 from the CPU vent is another innovation of the last 5 years of oxyfuel combustion development. The additional capture from the vent could result in a high capture rate of greater than 98% and could also minimize the impact of the air ingress in the boiler system. These options are developed by taking advantage of the quality of the vent gas from the CPU which is typically delivered at pressure (i.e. between ~15 -30 Bar_a) with high CO_2 and O_2 content.

Some of the processes presented by the different OEM vendors are described below:

- Air Products proposed the use of CO_2 membrane ("Prism") where the permeate, consisting of CO_2 and O_2, is recycled back to the boiler. It is claimed that with this equipment installed, the oxygen requirement from the ASU could be reduced by 3-5% [White, 2008, 2011].

- Linde proposed the use of PSA to further recover CO_2 from the vent gas of the CPU. The CO_2 rich gas recovered is recycled back to the dehydration unit of the CPU; whilst the remaining gas could be fed into the front end purification unit of the ASU. It is claimed that energy consumption of the CPU will increase by 6% as compared to the CPU without PSA installed. However, Linde has not reported the possible saving that could be gained in the ASU [Ritter, 2011(b)].

- Praxair proposed the use of VPSA to recover CO_2 from the vent of the CPU. The CO_2 rich gas recovered is recycled back to the sour CO_2 compressor just after the FGC. Praxair has yet to report the performance of this process [Shah, 2011].

- Air Liquide proposed the use of membranes to recover CO_2 from the vent of the CPU and the permeate is recycled back to the flue gas compressor situated at the warm part of the CPU [Lelerc et al, 2013].

The focus of development will be in the areas of the cycle improvement and process integration.

5.4.3.1. *Cost and energy consumption*

The vent stream is relatively small so that the costs of treatment equipment will be only a small part of the total plant cost. The vent stream leaves the CPU cold and at pressure and current designs extract some power from it by heating and then passing through an expander. The energy consumed in any extraction process will have to be balanced against any losses in this recovered energy. However the gains from increased CO_2 recovery and/or oxygen recovery are likely to outweigh this. The potential gains will be quite small, based on the Air products assessment of 3-5% reduction in ASU size a 2-3% reduction in LCOE may be possible.

5.4.3.2. Technology readiness level

All of the vent recovery technologies are proposals based on use of existing processes. Sufficient information on the processes is available to predict performance but until this is validated the proposals are at the stage of formulation of the application. On the basis that the applicable technologies have been used extensively in other gas processing applications, the technology readiness level is assessed as TRL-7. The scale up of some processes may need to be demonstrated.

5.5. Oxy-combustion for gas fired power plants

Oxy-combustion can be used in high temperature turbines, burning natural gas or gas produced by solid fuel gasification. Typical gas-fired oxyfuel cycles would have the following features:

- The combustor of the gas turbine is generally operated close to stoichiometric combustion using nearly pure oxygen mixed with recycled flue gas or steam.
- The main working fluid mainly consists of CO_2 or H_2O (or mixtures of both).
- The combustion would require oxygen that could range between 10 to 300 bar, and oxygen purity ranging from 95 to 99% - depending on the type of GT cycle and the combustor design of the turbo machinery used.
- If fired with natural gas, the CO_2 processing unit mainly consists of separation of water and CO_2. The amount of NOx present in the flue gas depends on the GT combustor design and the purity of oxygen used. However, if fired with syngas from gasification of coal or other solid fuels the CO_2 processing unit would require the removal of trace compounds such as SOx if sulphur compounds have not been removed upstream in the syngas treating plant.

From the literature, there are several cycles proposed or under development. Examples of oxyfuel cycles using CO_2 as the working fluid include the MATIANT [Mathieu and Nihart, 1999, 2000], Coolenerg [Staicovici, 2002], COOPERATE [Yantovski et al, 1996a; 1996b], and Allam [Allam et al 2013] Cycles. On the other hand, cycles using mainly water as the working fluid include CES Water [Andersson et al 2003, 2008; Marin et al, 2003; Pronske, 2013] and Graz cycles [Jericha et al, 2004]. Other hybrid cycles which do not require any ASU for oxygen production include the use of Chemical Looping [Ishida and Jin, 1994; 1998; Naqvi and Bolland, 2005] and AZEP cycle [Griffin et al, 2005; Moller et al, 2005]. Research using ITM and OTM technologies for oxygen production are being evaluated.

5.5.1. Clean Energy Systems (CES)

Among the cycles mentioned above the Clean Energy Systems (CES) cycle has been developed to the largest scale. The CES Water Cycle was developed using the adaptation of a rocket engine's combustor to provide the main gas generator for the oxyfuel cycle. The typical working fluid generated by the combustor is about 80% H_2O and 20% CO_2. The initial temperature of the combustor (i.e. first chamber) is maintained between 1650 and 1750C; and the operating pressure is generally in the range of 50 to 100 bar. Temperature is moderated in the cooling chamber downstream of the combustor/gas generator by water or steam injection to match the operating inlet temperature of the high pressure (HP) steam turbine (normally between 500-610C for current generation steam turbine, and up to 760C for future generation steam turbine). The pressure ratio of the current generation HP steam turbine is about 5. The working fluid is reheated in an external combustor to provide a working fluid with a turbine inlet temperature (TIT) matching the capabilities of the intermediate pressure (IP) gas turbine or OFT. Typical TIT could be in the range of 700 to 1750C depending on the operating inlet turbine temperature of the modified gas turbine to be used. The heat from the exhaust of the gas turbine is recovered via HRSG and the steam generated by the HRSG is delivered to the low pressure (LP) steam turbine; or the exhaust of the OFT could be used as the working fluid for the LP steam turbine (if temperature match the operating temperature of available steam turbine).

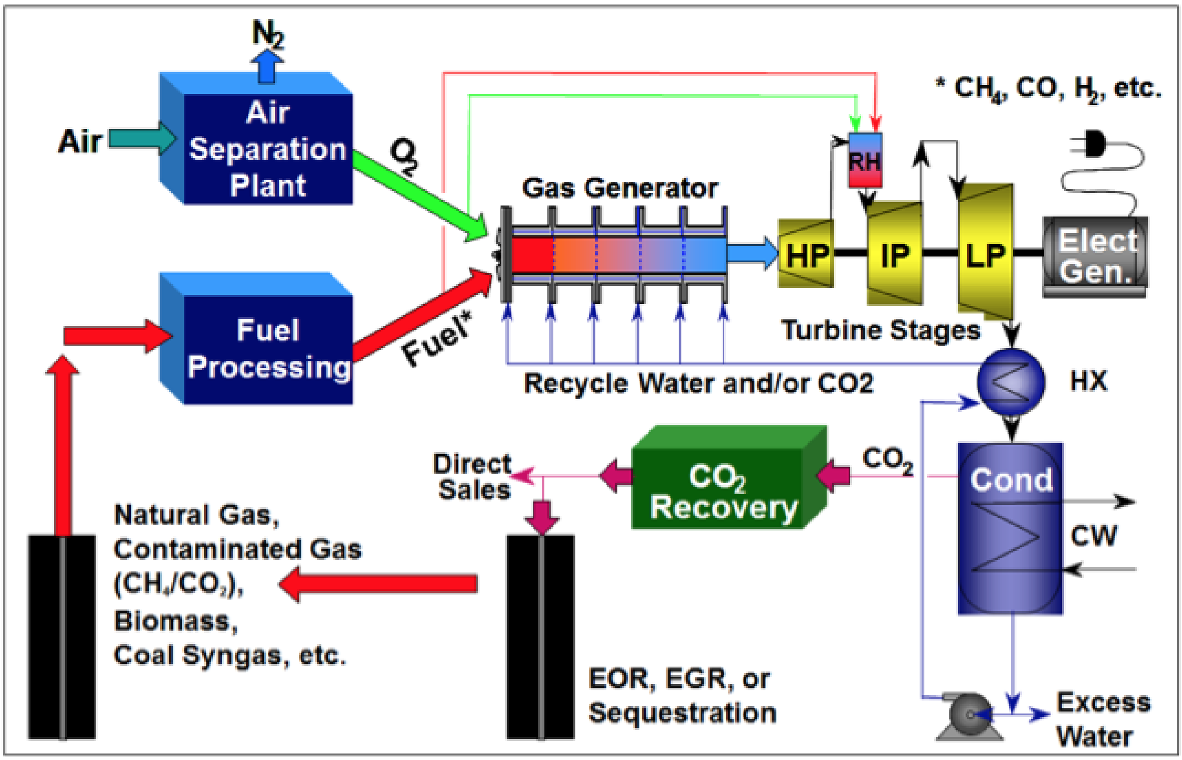


Figure 48 The CES cycle

A 200MWth high pressure combustor and a 43MWe turbine have been operated. Future development of this technology includes, but is not limited to, the following:

- Further demonstration of the reheat combustor and long term operation of a full scale turbine.
- Demonstration and validation of the sytems economic feasibility based on a large scale full chain power plant with CO_2 capture.
- The potential of the CES Water Cycle technology to improve its efficiency depends on the development of two main components namely: the HP steam turbine and the oxyfuel gas turbine to operate at higher inlet temperatures
- Demonstration of this technology using gaseous fuels other than natural gas. This should benefit industrial users that could use low calorific value off-gases or development of coal based systems using gasifiers to produce syngas.

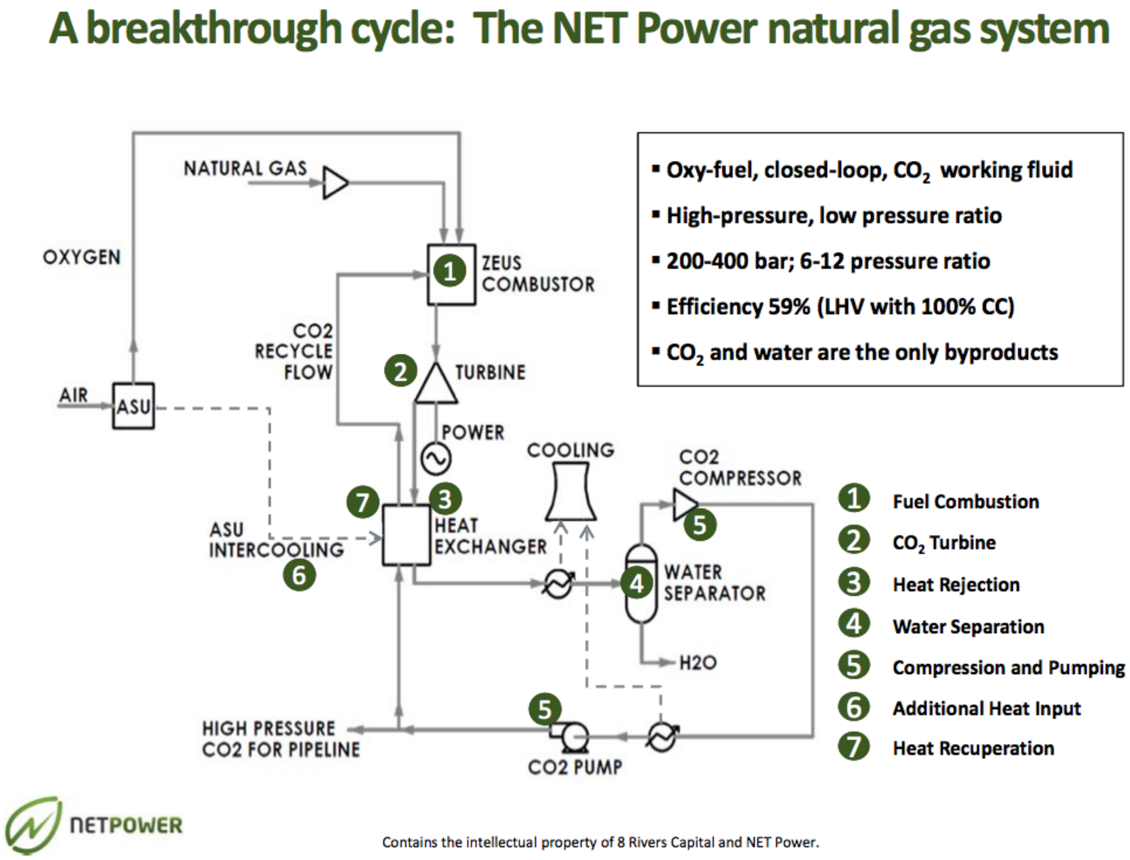
5.5.2. The Allam Cycle

The other cycles mentioned above except for the Allam Cycle have not yet progressed to any pilot demonstration.

The Allam Cycle is developed by NET Power in collaboration with Toshiba, CB&I and Exelon. Components of the Allam Cycle have been tested (i.e. combustors). The gas turbine has been designed and engineered with demonstration of at 25MW scale planned in the next two years at a site in Texas.

The Allam Cycle is based on supercritical CO_2 as the main working fluid. The fluid at a pressure of around 300bar is heated to 1100-1200C by combustion of fuel using high purity oxygen. The hot gas is then expanded in a turbine to typically around 30bar, after which it is cooled to near ambient temperature in a heat exchanger and water is separated. Some the remaining gas (mainly CO_2) is extracted as the net CO_2 output and the rest is re-pressurised in a gas compressor followed by a liquid pump before being heated, firstly to around 700C by heat exchange with the turbine exhaust gas and then in the combustor. The high pressure/high temperature heat exchanger and operation of the overall cycle are other important aspects which require demonstration.

The current challenge and near term development aim of this technology is the successful demonstration of the specially designed gas turbine using supercritical CO_2 as the working fluid. Important to the turbine development is the success of using CO_2 as the cooling medium in the turbo machinery.



A breakthrough cycle: The NET Power natural gas system

- Oxy-fuel, closed-loop, CO_2 working fluid
- High-pressure, low pressure ratio
- 200-400 bar; 6-12 pressure ratio
- Efficiency 59% (LHV with 100% CC)
- CO_2 and water are the only byproducts

1 Fuel Combustion
2 CO_2 Turbine
3 Heat Rejection
4 Water Separation
5 Compression and Pumping
6 Additional Heat Input
7 Heat Recuperation

Contains the intellectual property of 8 Rivers Capital and NET Power.

Figure 49 The Allam cycle flowscheme

5.5.3. Thermodynamic considerations

A key to obtaining high efficiency in novel oxy GT cycles is attaining high enough temperatures at the inlet to the turbo machinery. Modern gas turbines have been able to reach high inlet temperatures by a combination of advanced materials and advanced turbine blade cooling technologies. The use of inter-stage reheat is also a strategy which can be deployed. Some of the cycles proposed use quite different working fluids and differences in their properties can change the theoretically attainable efficiency. Some examples of the issues are – in cycles using mixtures of CO_2 and steam such as the CES cycle it is difficult to recover as much of the latent heat of evaporation of water in the cycle as occurs in partially condensing steam turbines. In the AZEP cycle temperature limitations in the oxygen separation membrane limit turbine inlet temperatures unless additional fuel is added to the inlet duct. Also the mass flow through the main power turbine is reduced because the fuel and oxygen do not pass through the main power turbine.

Oxy gas turbine cycles are being developed initially to consume natural gas. They thus have to compete with the very high efficiencies obtainable in NGCC plants which have already reached 60% without capture. Application of oxycombustion to natural gas suffers from the inefficiency that oxygen has to be produced to combust the hydrogen content as well as the carbon content of the fuel.

5.5.4. Cost and energy consumption

Cost estimates for alternative oxy-combustion power cycles are difficult to establish because they require development of new equipment. The easier driver to evaluate is that of overall thermal efficiency since simulation software can make reasonably accurate predictions of this. Care still needs to be taken to use appropriate parameters for equipment efficiencies and heat exchange temperature approaches to ensure these reflect practicality. Process conditions also need to respect material property limitations to avoid over optimistic predictions.

Efficiencies of 45-49% LHV are predicted for oxy-fuel combined cycle, water cycle and Graz cycle plants [Kvamsdal, 2007]. An efficiency of 59% LHV has been claimed for a natural gas fired Allam cycle with CO_2 capture, which is similar to the efficiency of a conventional natural gas combined cycle without capture [Allam, 2013]. A CCS plant which includes coal gasification and a syngas fired Allam cycle is claimed to have an efficiency of 50% LHV and a lower LCOE than pulverised coal and IGCC plants without CCS [Lu. 2014]. In this case the gasification plant does not include acid gas removal, instead SOx is removed downstream of the heat recovery heat exchanger. IEAGHG is currently undertaking a study to assess the performance and costs of oxy-combustion turbine cycles.

5.5.5. Current Status, technology readiness level and development requirements.

Most of the alternative cycles are proposals needing further development of the required hardware. Most of the alternatives are thus assessed as being at TRL-2. The main exception is the CES technology where significant progress has been made in testing at moderate scale. This is therefore assessed as being at TRL-5. Despite the size of the systems tested there is still a need to proceed to test systems at the higher temperature and pressure conditions needed for the process to be competitive. A fully integrated test at “commercial” process conditions is also needed.

One of the key areas of development for the Oxy-GT cycles involves the right selection of the ASU cycle suitable to deliver medium to high pressure oxygen with purity ranging from 95-98%. Two important components of the ASU would require significant attention – this involves the right selection of the main air compressor which in some cases is a necessary part of the integration between the power plant and oxygen production unit. The second element is the scaling up of the LOX pumps that could potentially provide additional improvement to the efficiency of the ASU.

Development of the CPU suitable for the Oxy-GT will also be the focus of future work. This is very dependent on the oxy-GT cycle. Depending on the trace elements (i.e. NOx, SOx) in the CO_2 rich flue gas, the CPU design could only involve a dehydration unit but may also involve pre-treatment of the CO_2 rich gas. Cryogenic separation of the inerts may not be necessary but this depends on the CO_2 purity required by for CO_2 transport and storage.

6. Solid looping technologies

Solid looping technologies capture CO_2 at high temperature in cyclical processes using either circulating or fixed beds of solids. High-temperature solid looping cycles involve the use of a solid carrier to transfer either CO_2 or O_2 from one reactor to another.

In calcium/carbonate looping (CaL), usually lime (CaO) captures CO_2 from a gas mixture with the sorbent then being regenerated to yield a pure stream of CO_2. Limestone is abundant and cheap but more effective and durable synthetic alternatives are also being developed. In recent years considerable advances have been made in combating loss of reactive capacity and attrition of the sorbent after a number of cycles to the point that these are no longer barriers to implementation. Besides, it is possible to use the spent sorbent to produce cement. Post-combustion CO_2 capture is the main area of application for CaL (see Figure 50).

Chemical looping combustion (CLC) is a method of indirect, oxy-combustion (compare Figure 50), where fuel and air are never mixed. A metal oxide transports oxygen from the air to the fuel, yielding a pure stream of CO_2 and H_2O, which can then be easily separated and the CO_2 subsequently stored or utilised. CLC inherently avoids costly gas separation steps. Therefore, CLC is one of the most energy-efficient approaches to capture CO_2 from power production or fuel upgrading. A key objective is to develop this technology to be able to completely combust coal, which would yield a CO_2 capture process whose only energy penalty is the CO_2 compression energy.

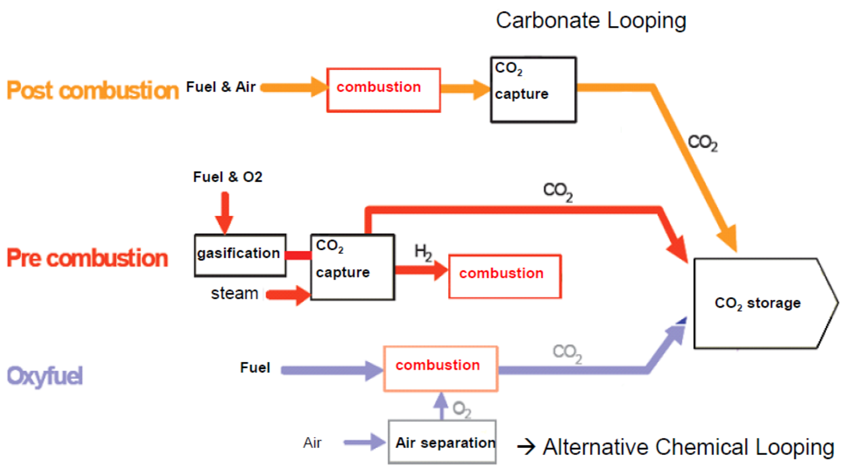


Figure 50 Location of CaL and CLC in the CCS chain [Epple 2011]

Alternatively, there are a number of CaL and CLC processes that can produce H_2 or syngas from hydrocarbon-based fuels, while simultaneously producing a pure CO_2 stream.

Solid looping technologies have advanced considerably in the last few years and recently several large pilot plants have been constructed and brought into operation. The next important step is the demonstration of these technologies at industrial scale and the generation and validation of techno-economic performance data, which is still limited.

6.1. Calcium/carbonate looping (CaL)

CaL generally consists of two main steps:

Carbonation reaction:

$$CaO(s) + CO_2(g) \rightarrow CaCO_3(s) \qquad \Delta H^{700°C,\ 1bar} = -170\ kJ/mol \qquad (1)$$

Calcination reaction:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \qquad \Delta H^{900°C,\ 1bar} = +165\ kJ/mol \qquad (2)$$

During carbonation (1), CaO is brought into contact with a flue gas containing CO_2 at approximately 650-700°C. CaO and CO_2 react to form $CaCO_3$, thus reducing the CO_2 concentration in the flue gas.

In the calcination step (2), $CaCO_3$ is fed into a calciner, where it is heated to 850-950 °C and will thermally decompose into CO_2 and CaO. The almost-pure stream of CO_2 can be removed and purified so that it is suitable for storage or use. The regenerated CaO is sent back to the carbonator. Due to the degradation of the sorbent, a make-up stream of $CaCO_3$ is necessary. Figure 51 shows the scheme of a standard CaL process.

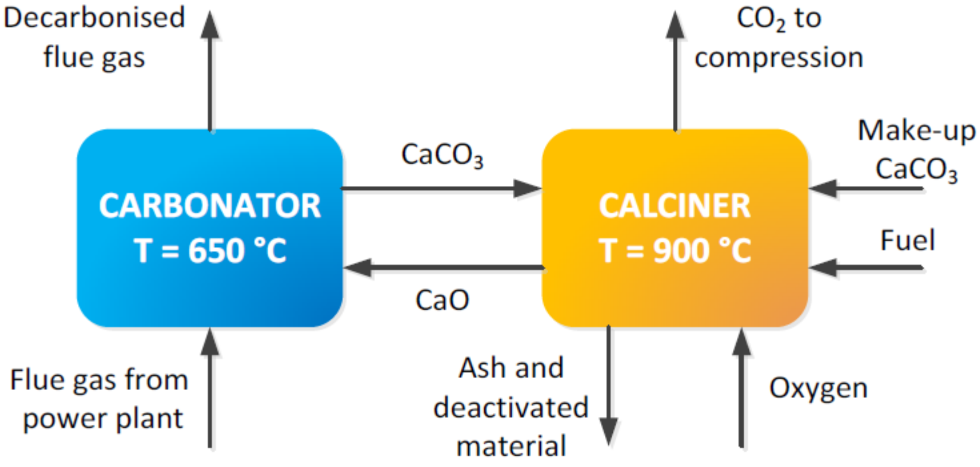
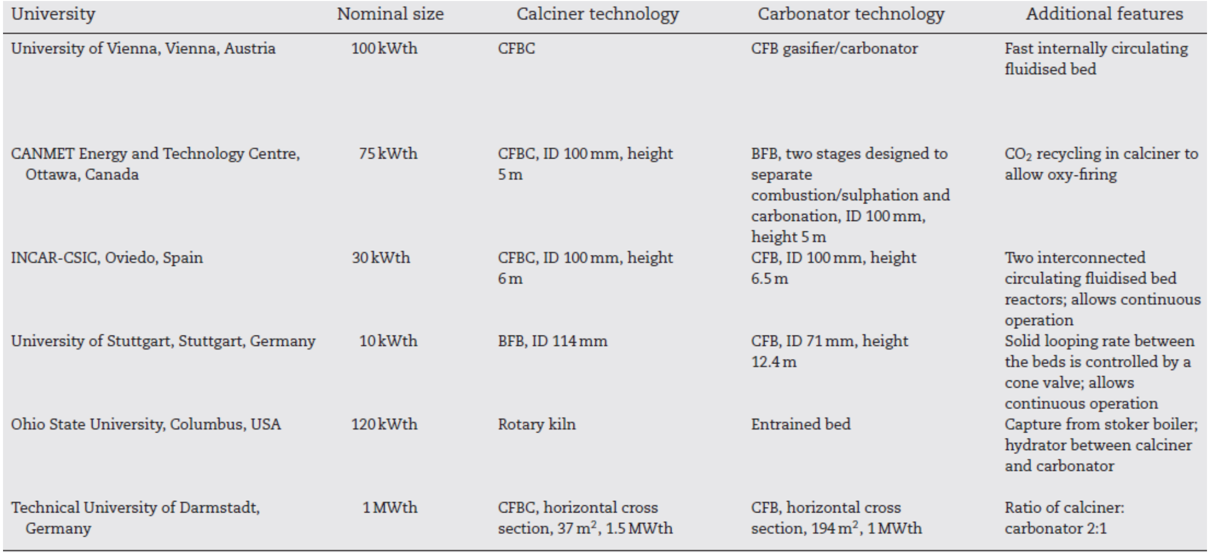


Figure 51 Scheme of a standard calcium looping process [Epple 2013]

6.1.1. *Current status*

Figure 52 is an overview of the CaL pilot plants that were in operation in 2011. Please note that the table is missing the 1.7 MW$_{th}$ pilot plant of CSIC-INCAR in Spain [Arias 2013], which is in operation since 2011/2012. The concept of post-combustion CaL, in continuous mode of operation, has been successfully proven with two interconnected circulating fluidised beds (CFBs) at the 1.7 MW$_{th}$ scale. In 2012, ITRI opened a 1.9 MW$_{th}$ pilot plant in Taiwan [Chang 2013]. TU Darmstadt has a 1 MW$_{th}$ pilot and is currently undertaking design studies for a 20 MW$_{th}$ scale-up [Junk 2014].



University	Nominal size	Calciner technology	Carbonator technology	Additional features
University of Vienna, Vienna, Austria	100 kWth	CFBC	CFB gasifier/carbonator	Fast internally circulating fluidised bed
CANMET Energy and Technology Centre, Ottawa, Canada	75 kWth	CFBC, ID 100 mm, height 5 m	BFB, two stages designed to separate combustion/sulphation and carbonation, ID 100 mm, height 5 m	CO$_2$ recycling in calciner to allow oxy-firing
INCAR-CSIC, Oviedo, Spain	30 kWth	CFBC, ID 100 mm, height 6 m	CFB, ID 100 mm, height 6.5 m	Two interconnected circulating fluidised bed reactors; allows continuous operation
University of Stuttgart, Stuttgart, Germany	10 kWth	BFB, ID 114 mm	CFB, ID 71 mm, height 12.4 m	Solid looping rate between the beds is controlled by a cone valve; allows continuous operation
Ohio State University, Columbus, USA	120 kWth	Rotary kiln	Entrained bed	Capture from stoker boiler; hydrator between calciner and carbonator
Technical University of Darmstadt, Germany	1 MWth	CFBC, horizontal cross section, 37 m^2, 1.5 MWth	CFB, horizontal cross section, 194 m^2, 1 MWth	Ratio of calciner: carbonator 2:1

Figure 52 Summary of CaL pilot plants [Dean 2011]

6.1.2. *Performance and cost*

According to [Epple 2013] and [Kremer 2013], the electrical efficiency of a state-of-the-art coal-fired power plant integrating post-combustion CO$_2$ capture by CaL lies in the range of

39-40%. Due to the low energy penalty, (~6%-points efficiency drop incl. CO_2 compression or ~3%-points excl. CO_2 compression) the technology is particularly suited for the retrofit of existing plants. The process efficiency can be further improved by integrating an indirectly heated calciner. More information on this indirectly heated CaL process is available in section 6.2.

CO_2 capture efficiencies of 80-90% were achieved in a CFB carbonator reactor operating with “standard” conditions [Arias 2013]. [Kremer 2013] reports operation of a 1 MW_{th} pilot plant with total CO_2 capture rates above 90% and [Epple 2013] gives CO_2 avoidance costs of ~20 €/tCO_2 as a first estimate for the process. This number is in agreement with a general economic projection of ~20 US$/t$CO_2$ that [Anthony 2011] suggests. [Abanades 2007] investigated the economics of the CaL cycle and calculated a likely range of costs from 7.1 US$/t$CO_2$ to 31.2 US$/t$CO_2$ avoided. [MacKenzie 2007] estimated the cost of CO_2 avoided at 19 US$/t$CO_2$. Their study included a sensitivity analysis and identified the cost of limestone and the assumed Ca/C ratio as having the most significant influence on the cost (see Figure 53).

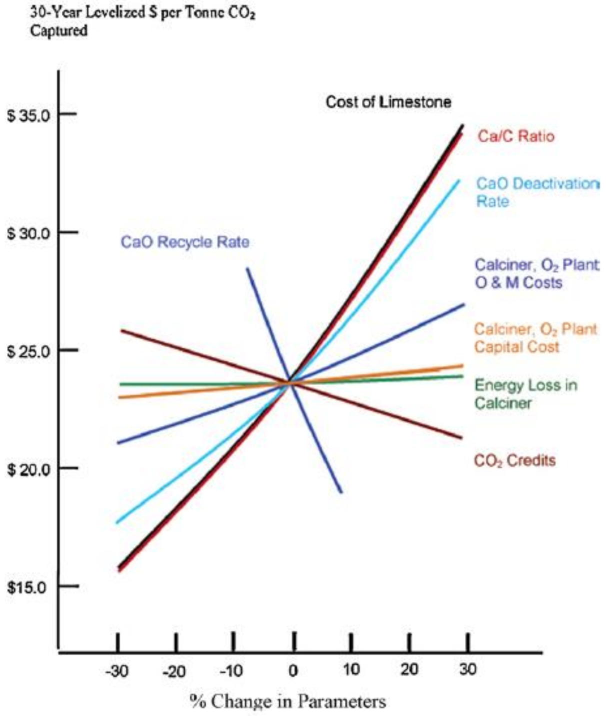


Figure 53 Sensitivity analysis showing the impact of varying critical cost parameters by ±30% on CO_2 capture cost [MacKenzie 2007]

A study by [Dean 2011] summarises the published cost data for CaL up to 2011. The authors conclude that in all cases studied the cost of CO_2 capture remained competitive (i.e. < 29 US$/t$CO_2$). However, they did not investigate cost data for the integration with cement manufacture, which is discussed later in this report.

6.1.3. Technology readiness level

Recent results from the MW scale pilot plants have reported good steady state performance in line with expectations. The 1.7 MW_{th} pilot at La Pereda has been able to use coal and oxygen as the fuel for the calciner, effectively simulating the fully integrated system. The technology readiness level is assessed as TRL-6. Use of this technology as a retro fit is possible but increases the overall plant capacity by 30-40%. The technology is thus most appropriate where there is a need for repowering to increase capacity or new build to replace retiring capacity.

6.2. CaL for combustion: an indirectly heated CaL process

[Junk 2013] and [Epple 2013] propose an indirectly heated CaL process, where the heat for the calciner is supplied by an external combustor via heat pipes, so no oxygen is needed for firing the calciner (see Figure 54 for the layout of the process and Figure 55 for the design of the integrated heat exchanger).

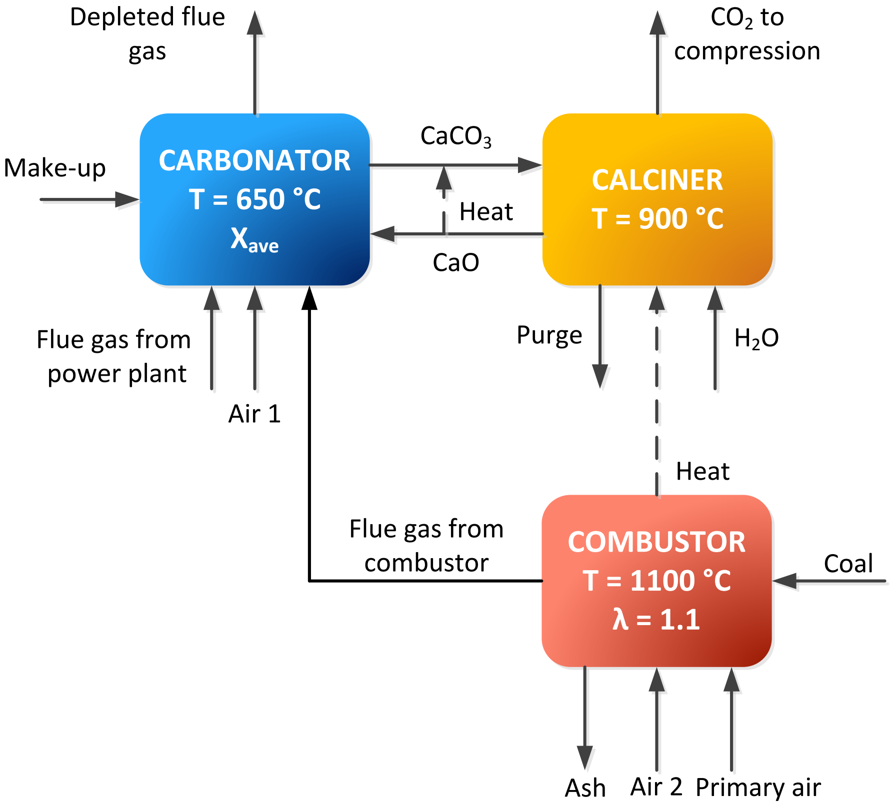


Figure 54 Process scheme for indirectly heated carbonate looping [Junk 2013]

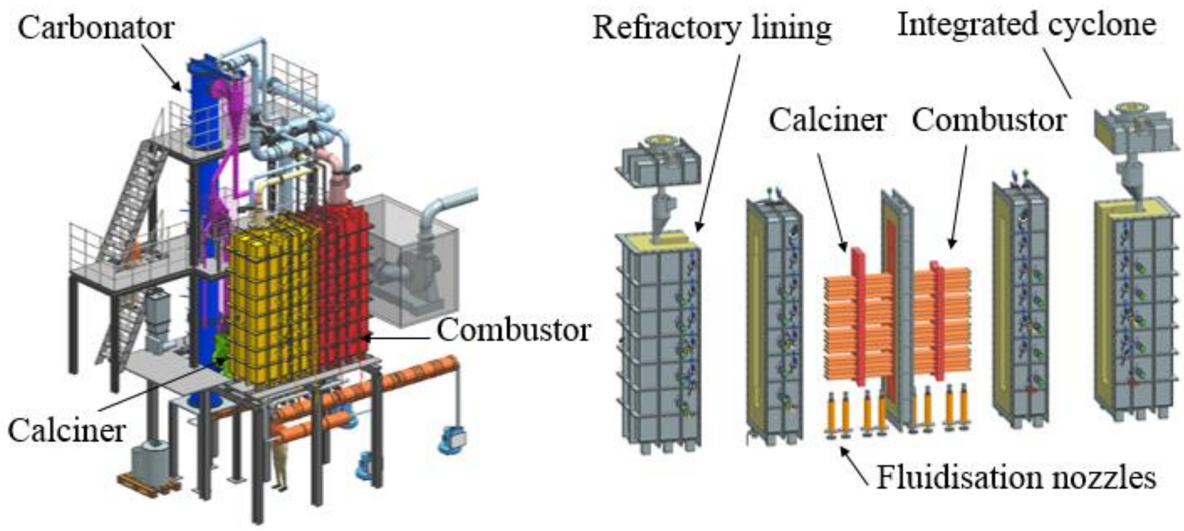


Figure 55 Left: design of the 300 kW$_{th}$ test facility; right: design of the heat exchanger [Junk 2013]

6.2.1. Performance and cost

The authors report low sorbent attrition rates in the calciner and low sorbent deactivation rates. Because there is no coal present in the calciner, few additional impurities (e.g. sulfur, ash) are brought into the system, which reduces the flow of circulating solids and facilitates the further utilization of deactivated sorbents. Solid flux investigations showed that the heat pipes do not significantly influence the particle flow through the calciner and the required solids mass flow through the reactor can be achieved.

Because the air separation step in a standard CaL process accounts for a large amount of the energy penalty (2%-points out of the total of 3%-points excl. CO_2 compression), the indirectly heated process will have a lower energy penalty of ~1 %-point.

6.2.2. Current status, technology readiness level and development requirements

A 300 kW$_{th}$ test rig has been designed and the first campaign is scheduled for the end of 2014 [Reitz 2014].

Successful operation of the pilot plant with indirect heating of the calciner will move this technology towards TRL-6. At present, the concept of the individual components is tested although the use of heat pipes in this type of application may still need validation. There may also be technical and engineering issues in scaling up the heat pipes, particularly if much longer pipes are needed at larger scale. The indirectly heated calciner version of CaL is assessed as being at TRL-3 subject to successful testing in the new pilot plant.

A retrofit of the process is generally possible but causes big plant sizes, thus a new-build is more appropriate.

6.3. CaL for H_2 production

At present, most H_2 (i.e. 96%) is produced from fossil fuels, resulting in an equivalent amount of CO_2 being released to the atmosphere. Given the enormous increase in production that would be necessary to support a transition to a H_2 economy, there is clear scope for improved methods in order to decarbonise this sector.

6.3.1. *Performance and cost*

[Connell 2013] assessed the techno-economics of the CaL process (CLP) for three different H_2 and electricity production technologies: coal-to-H_2, steam methane reforming (SMR) and integrated gasification combined cycle (IGCC). In each of the coal-to-H_2, SMR, and IGCC cases evaluated, use of CaL results in a 9–12% reduction in cost of H_2 (COH) or levelised cost of electricity (LCOE), when compared with the use of conventional CO_2 capture and water-gas shift (WGS) technologies (see Tables 12 and 13). The reason for this economic advantage is the large amount of high-quality heat produced in the processes that is available to raise steam for electricity generation. Although CaL can reduce the cost of producing H_2 from coal, the resulting cost is still about 26% greater than the cost of H_2 produced from natural gas using conventional WGS and CO_2 capture. In the study, the lowest-cost route to H_2 production with CO_2 capture is the SMR with CaL case.

Table 12 Techno-economics of the coal-to-H_2 and SMR cases [Connell 2013]

	Coal-to-H_2 case		SMR case	
	Base plant	CLP plant	Base plant	CLP plant
First-year capital (\$/kg H_2)	\$2.28	\$2.61	\$0.62	\$0.97
Fixed O&M (\$/kg H_2)	\$0.44	\$0.60	\$0.17	\$0.27
Fuel (\$/kg H_2)	\$0.36	\$0.55	\$1.22	\$1.40
Electricity (\$/kg H_2)[a]	−\$0.03	−\$1.14	\$0.14	−\$0.70
CO_2 emissions (\$/kg H_2)	\$0.06	\$0.00	\$0.03	\$0.00
Other variable O&M (\$/kg H_2)	\$0.04	\$0.14	\$0.02	\$0.05
First-year COH (\$/kg H_2)	\$3.15	\$2.77	\$2.20	\$1.99
First-year COE (\$/MW h)	\$105.00	\$92.07	\$105.00	\$95.27

[a] Computed using an electricity price equal to the total COE value shown in the table.

Table 13 Techno-economics of the IGCC cases [Connell 2013]

	Base plant	CLP plant
First-year capital (\$/MW h)	\$59.00	\$51.20
Fixed O&M (\$/MW h)	\$22.38	\$18.88
Coal (\$/MW h)	\$17.12	\$16.86
CO_2 emissions (\$/MW h)	\$2.71	\$0.15
Other variable O&M (\$/MW h)	\$1.76	\$3.59
First-year COE (\$/MW h)	\$102.97	\$90.68

[Dean 2011] also gives an overview of the possibilities of H_2 production with methods of CaL cycles. These processes, as well as the ones in Connell 2013, offer significant potential for efficiency and economic improvements.

6.3.2. *Future developments*

[Connell 2013] conclude that additional research is required to resolve technical uncertainties related to commercial application of these technologies, as they usually involve higher technical complexity.

The following sections briefly describe three exemplary CaL technologies for H_2 production.

6.4. Combined shift-carbonation

Combined shift-carbonation is an advanced process coupling the carbonation reaction (3) with the WGS (4) to produce H_2:

$$CaCO_3(s) = CaO(s) + CO_2(g) \qquad \Delta H^0 = +178\ \text{kJ/mol} \qquad (3)$$

$$CO(g) + H_2O(g) = CO_2(g) + H_2(g) \qquad \Delta H^0 = -41\ \text{kJ/mol} \qquad (4)$$

6.4.1. *Performance and cost*

The removal of gaseous CO_2 as solid $CaCO_3$ shifts the CO conversion and thus increases the output of H_2.

6.4.2. *Current status, technology readiness level and development requirements*

The use of CaL for H_2 production is at an early stage of investigation. The principles are understood and several concepts have been proposed. The technology readiness level is assessed as TRL-1.

The process suffers from the same issues as the standard CaL process, i.e. the degradation of the sorbent through multiple cycles, which will lead to a decrease in H_2 productivity and therefore affects the efficiency of the process.

6.5. Sorption enhanced reforming (SER) and sorption enhanced water gas shift (SEWGS)

SER of hydrocarbons for H_2 production is a very complex process combining SMR according to (5) with the carbonation (3) and the water-gas shift reaction (4) in a single step.

$$CH_4(g) + H_2O(g) \leftrightarrow 3H_2(g) + CO(g) \qquad \Delta H^0 = +206\ \text{kJ/mol} \qquad (5)$$

6.5.1. *Performance and cost*

This process also exploits the advantage of removing CO_2 from the reaction system to enhance conversion of CO and can produce a concentrated stream of $H_2 > 98$ vol%. [Ortiz 2001] report potential energy savings of SER compared to standard SMR to be in the order of 20%.

6.5.2. *Current status, technology readiness level and development requirements*

The process has been demonstrated at lab-scale using a pressurised fixed-bed reactor by [Balasubramanian 1999], reporting a product gas consisting of 94.7 vol% H_2.

The SEWGS process has been covered in the chapter on pre-combustion technologies. The SER process principle has been demonstrated some time ago but no further work appears to have been done. The technology readiness level for SER is assessed as TRL-1.

6.6. The ENDEX process

The ENDEX process by Calix, as described in [Sceats 2009] and [Ball 2010], is a “reversed” application of the conventional CaL technology, where calcination is carried out at a lower temperature (650–760°C) than the carbonation (760–850°C). This together with the minimisation of the CO_2 pressure in the calciner eliminates some of the key technological challenges of CaL processes (i.e. decay in CO_2 capture capacity through multiple cycles, process heat integration and sintering). Figure 56 shows the principle of the ENDEX configuration.

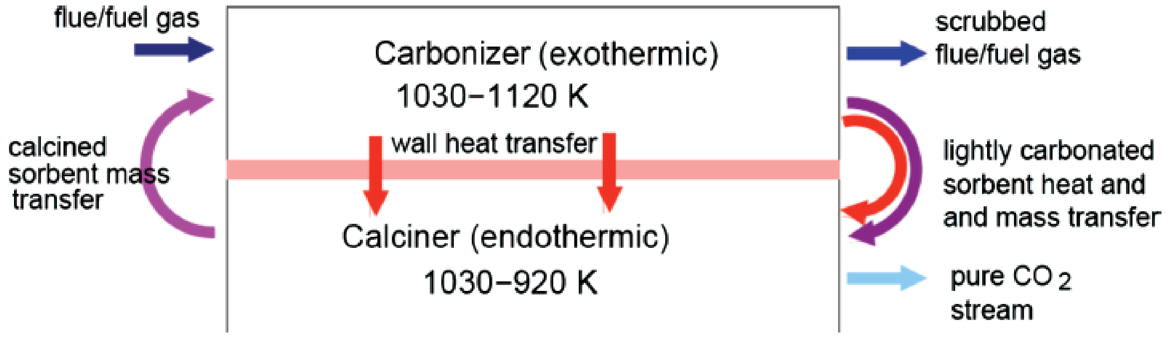


Figure 56 The ENDEX process [Ball 2010]

6.6.1. Performance and cost

[Sceats 2009] reports 13.7 US$/t$CO_2$ avoided for a syngas fuelled ENDEX process and 23.1 US$/t$CO_2$ for natural gas fuelled. The cost for flue gas compression is 5.9 US$/t$CO_2$, resp. 5.5 US$/tCO_2. Calix's aim is to achieve > 90% CO_2 capture, < 6% loss of power/efficiency and a capture cost < 12 US$/t$CO_2$ avoided.

6.6.2. Current status, technology readiness level and development requirements

Some of the issues surrounding the process may be resolved with further experimental work and experience with a (planned) 10 MW_{th} demonstrator.

According to [Dean 2011], a number of engineering concerns remain. The novel process configuration requires transport of sorbent particles through a pressure gradient and pressurisation of the sub-atmospheric stream of CO_2 before transport and storage. The requirement to compress the flue gas imposes an additional energy penalty. The cycle requires two pressure changes, one to a higher pressure and one back to the lower pressure. To be efficient there should be energy recovery from the pressure reduction. Apart from cyclic pressurisation through a lock hopper or similar arrangement, there are no other technologies for pumping solids over the pressure differential required. Equally, there is no equipment currently able to let down a stream of solids with energy recovery. Thus whilst the thermodynamics are sound the application using a solid flowing medium is not considered practical from an engineering standpoint.

The ENDEX technology appears to be largely theoretical and significant hurdles in formulation of an application have to be overcome. TRL-1 seems appropriate.

6.7. CaL integration into cement production

The cement production process emits between 0.6 and 1 kg of CO_2 per tonne of cement [ECRA 2007], and the energy consumption of producing a tonne of clinker ranges from 3.1 to 7.5 GJ [CEMBUREAU 1999]. The exhausted CaO from a CaL process can be used as a raw material in cement/clinker production, as limestone represents ~85 wt% of the raw feed.

6.7.1. Performance and cost

[Dean 2011] cites 19 US$/t$CO_2$ avoided for such an integrated process. This is highly competitive with other figures for cost of CO_2 avoided determined in an economic study of

CO_2 capture in the cement process using amines (144 US$/tCO$_2$) and using an oxy-fired kiln configuration (54 US$/tCO$_2$) by [Barker 2009]. [Dean 2011] concludes CaL integration can reduce the energy requirement for clinker manufacture from 3.1 GJ/t by approximately 50%, so there is the possibility for significant decarbonisation.

[Rodriguez 2008] state it would be possible to reduce the CO_2 emissions from a cement plant by as much as 60%, with a cost of around 19 US$/tCO$_2$ avoided.

[Romano 2013] investigated integration of CaL into a state-of-the-art power plant and cement manufacture (see Figure 57). The reference cement plant produces 4050 t/d of clinker with a state-of-the-art dry process. Estimates indicate that complete substitution gives a reduction of up to 70-75% of the thermal input and up to 85% of CO_2 emissions, with respect to the reference plant.

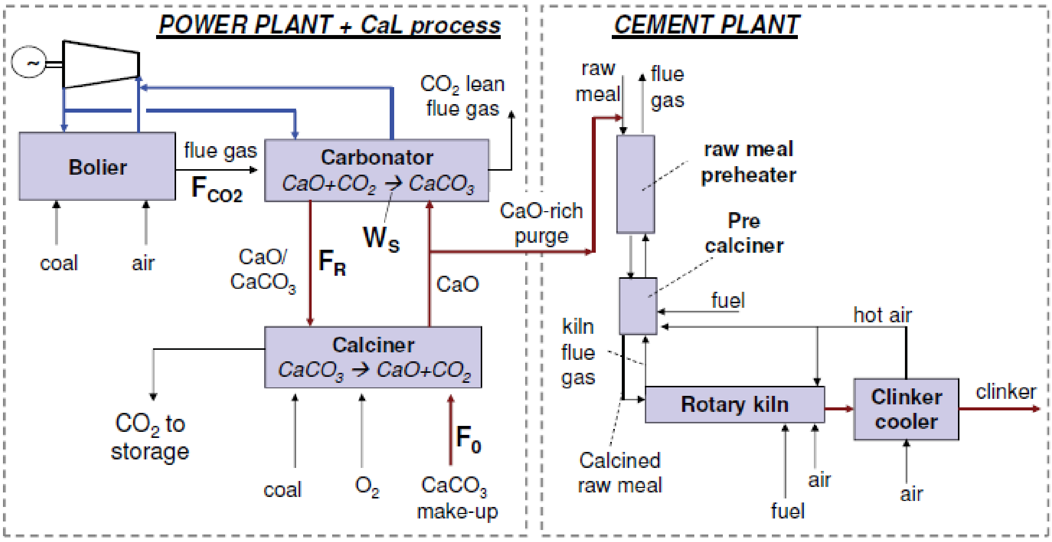


Figure 57 Integration of CaL process with power and cement plant [Romano 2013]

For the economic analysis the authors assumed a cost of 7 €/tCO$_2$ for transport and storage. They chose to calculate the LCOE by assuming different values of the carbon tax (instead of calculating the cost of the CO_2 avoided, which can provide misleading results for low CO_2 capture cases). In COE-1 scenario, the selling price of cement increases by the same amount of the cost associated to the carbon tax in a cement plant without CO_2 capture. In COE-II, the selling price of cement is unaffected by the carbon tax, and thus the additional cost of the CO_2 emitted from the stack of the cement plant is entirely charged on the cost of the electricity. The authors expect that any real economic scenario would be intermediate between these two and conclude that 27 €/tCO$_2$ is the minimum cost of CO_2 avoided expected for the system. Figure 58 shows the detailed results of this economic analysis.

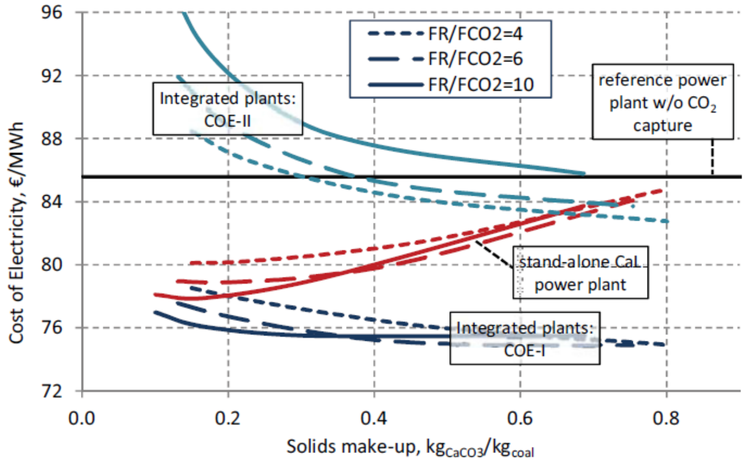


Figure 58 COE for cement plant integration for a carbon tax of 40 €/tCO_2 [Romano 2013]

[Ozcan 2012] did a simulation study of a cement plant with CaL and reports a gross power generation efficiency of 46% with CO_2 capture rates between 92–99%. One of the cases studied in their work showed an energy consumption of 5.3 GJ/tCO_2, compared to a value of 4.6 GJ/tCO_2 for an integrated MEA process. With heat recovery, the resulting energy consumption would decrease to 2.3 GJ/tCO_2.

6.7.2. *Current status, technology readiness level and development requirements*

ITRI is operating a 1.9 MW_{th} pilot plant with flue gas from a cement plant in Taiwan since mid of 2013 [Chou 2013].

The integration and use of waste CaL sorbent in the clinker are at an early stage of development. However, the main CaL system can be considered as at the same stage as that intended for a conventional power plant, which was assessed as TRL-6. The integration aspects are thus assessed at TRL-1. It should be noted that use of waste sorbent derived from a power generation process with CaL in cement clinker capture could potentially enhance the economics of the power plant. A key concern for using spent sorbent from CaL in a cement plant are trace elements, their incorporation into the clinker and their effects on the production process and on cement performance [Bhatty 2003].

6.8. Chemical looping combustion (CLC)

In CLC, fuel and combustion air never come into contact with one another, creating a CO_2 exhaust gas stream not diluted with N_2. Figure 59 shows a scheme of a standard CLC process. The reactions for the oxidation and reduction step of the metal oxygen carrier (MeO) are (6) resp. (7). Simply condensing out the water vapour from the fuel reactor exhaust gas stream results in a CO_2 stream with >99% purity.

Oxidizer (air reactor):

$$Me_xO_{y-1} + 1/2O_2 \rightarrow Me_xO_y \tag{6}$$

Reducer (fuel reactor):

$$C_nH_{2m} + (2n+m)Me_xO_y \rightarrow nCO_2 + mH_2O + (2n+m)Me_xO_{y-1} \tag{7}$$

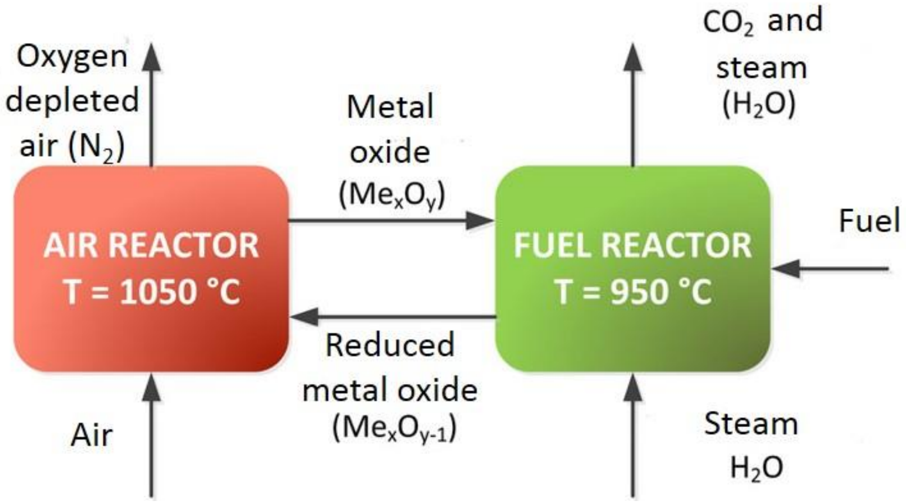


Figure 59 Scheme of a standard CLC process [Epple 2013]

Several publications discuss the advantages and disadvantages of CLC technologies [Spigarelli 2013, DOE/NETL 2013, Adanez 2012, Moghtaderi 2012]. A summary is provided below.

Advantages

- Air separation unit (ASU) is not required. This eliminates large capital, operating, and energy costs associated with O_2 generation.
- CO_2 stream is not diluted with N_2, which makes for an easier, in-situ CO_2 separation.
- Since no energy is required for the separation of O2 or CO2, CLC potentially has the lowest efficiency penalties among all CO2 capture technologies.
- Inherent reduction of NOx emissions since air and fuel never contact one another.
- Process can be applied to any form of fuel (i.e. solid, liquid or gas).
- CFB technology is relatively mature.

Challenges

- Pressure of the two reactors must be the same to prevent air leakage to fuel reactor.
- Reduced reduction rate of the MeO after the first cycle. Reasons are the deactivation of the MeO due to unburned carbon deposition on the surface of the particles and attrition.
- Heat integration and ash separation.
- Sulfur compounds will react to form metal sulphides, so the fuel needs desulphurisation before entering the fuel reactor.
- Technology is in the R&D phase, with no demonstrations or commercial plants in operation.

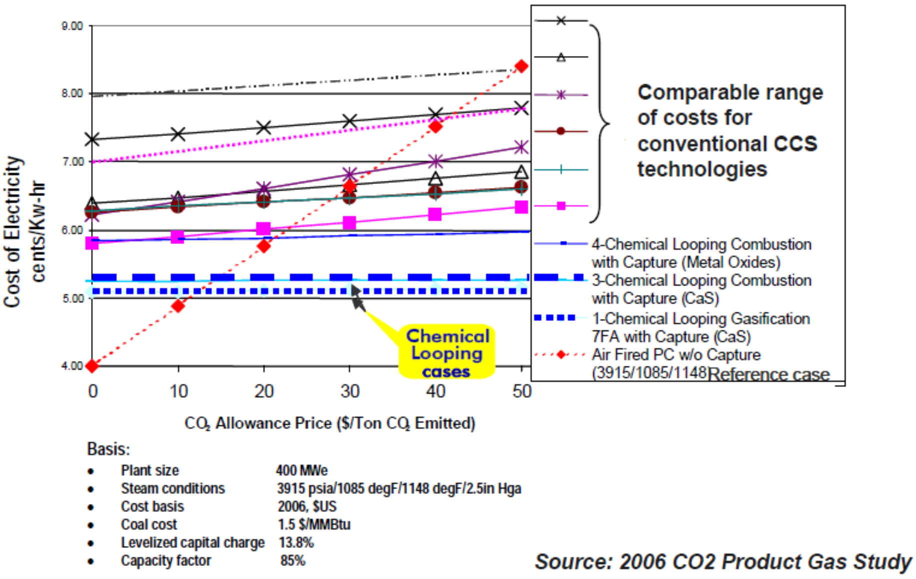
Chemical looping offers a high degree of flexibility, as it can produce either steam for electricity generation, or hydrogen, both in combination with CO_2 capture. In this context, chemical looping reforming (CLR) technologies can reduce the cost of CO_2 capture whilst simultaneously producing H_2. Two interesting methods are steam reforming integrated with chemical looping combustion (SR-CLC) and autothermal chemical looping reforming (a-CLR), which are discussed later in this section.

[Spigarelli 2013] concludes that compared to other CO_2 capture technologies, CLC is the furthest behind in terms of commercial development.

6.8.1. Performance and cost

For a coal-fired CLC process, [Epple 2011] reports that the potential electrical efficiency can reach values up to 42% depending on steam flow for fluidisation of the fuel reactor. The authors discuss that CLC is a promising option for new power plants, rather than for retrofit, and estimate the CO_2 avoidance costs to be ~10 €/tCO_2.

In 2006, Alstom compared the cost of electricity (LCOE) of CLC technologies with conventional CCS technologies [Alstom 2013]. Figure 60 shows that CLC has the potential for significantly lower LCOE than all other investigated CCS technologies and does not seem to be sensitive towards the CO_2 allowance price.



Source: 2006 CO2 Product Gas Study

Figure 60 LCOE for chemical looping compared to conventional CCC technologies [Alstom 2013]

The issue of estimating costs has been addressed [Lyngfelt 2014a], suggesting that costs could best be compared with those for the similar CFB technology. Based on the performance of a 100 kW CLC unit projections for a 410 MW_e unit were prepared. A key assumption is that volatiles would not undergo complete combustion, with between 5% and 15% of the oxygen demand having to be met from an ASU. Recent results in the 100 kW unit suggest that addition of manganese ore can significantly reduce this extra demand for oxygen by increasing volatiles conversion. The final oxidation would have to be done in an oxy polishing unit downstream of the main fuel reactor. The air reactor and fuel reactor each would differ from a typical CFB and suggestions as to how the costs could be ratioed for these differences are proposed. In particular, the fuel reactor would be adiabatic and the usual steam raising walls would need to be replaced with more expensive insulated walls. The other significant parasitic energy consumers are CO_2 compression and solids circulation.

6.8.2. *Thermodynamic and chemical reaction considerations*

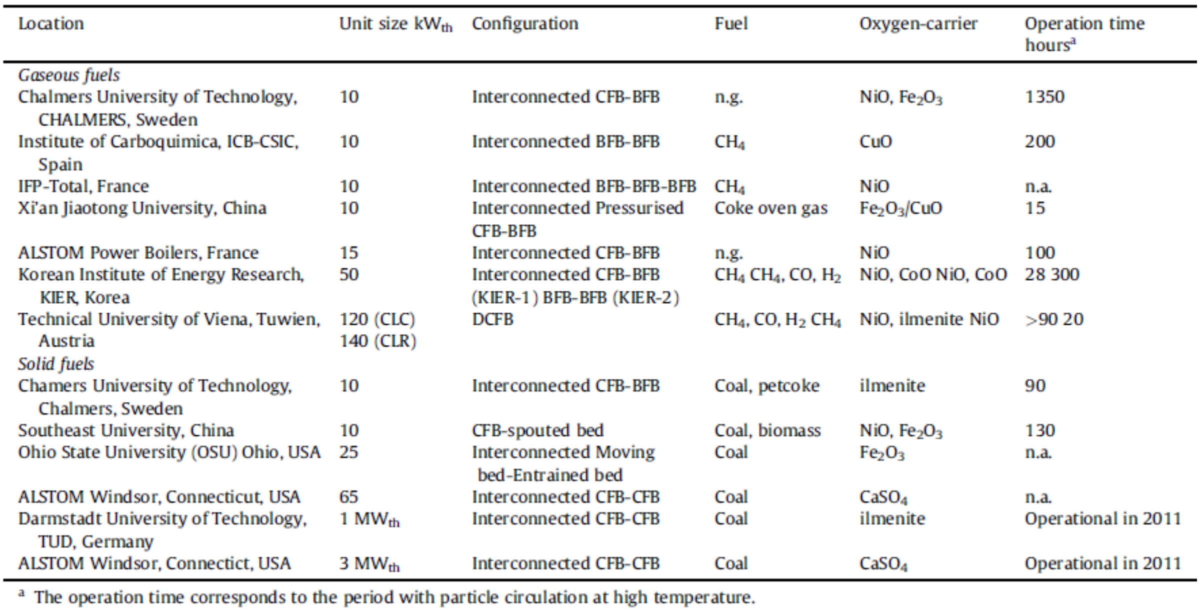
By using the chemical potential of the combustion reaction in two stages, the energy required for separation is effectively derived directly from the combustion reactions eliminating energy intensive separation processes. This can be done without penalty as long as the top temperatures of the power generation working cycle are maintained. For coal-fired plants running a steam cycle where top temperatures are currently limited to below 700°C this can easily be achieved. However, gas-fired plants operate with turbine inlet temperatures up to 1500°C and this may be even increased with new materials developments. CLC fuel reactor temperatures cannot match this and hence are unlikely to compete in gas-fired power generation applications. The exception is locations where natural gas is the preferred fuel for steam generation, notably for heavy oil recovery in remote locations.

6.8.3. *Current status, technology readiness level and development requirements*

[Spigarelli 2013] provides an overview of CO_2 capture technologies, including CLC. The authors report that the operating temperature and pressure of the reactors may range from 800 to 1200°C and 1 to 69 atm, depending heavily upon the type and size of oxygen carrier used. Common oxygen carriers for CLC processes include iron, nickel, cobalt, copper, manganese, and cadmium.

One important advantage of the use of a fluidized bed configuration for the CLC process is that CFB technology is mature. Table 14 summarises the currently existing CLC pilot plants.

Table 14 Summary of chemical looping pilot plants [Adanez 2012]



Location	Unit size kW_{th}	Configuration	Fuel	Oxygen-carrier	Operation time hours[a]
Gaseous fuels					
Chalmers University of Technology, CHALMERS, Sweden	10	Interconnected CFB-BFB	n.g.	NiO, Fe_2O_3	1350
Institute of Carboquimica, ICB-CSIC, Spain	10	Interconnected BFB-BFB	CH_4	CuO	200
IFP-Total, France	10	Interconnected BFB-BFB-BFB	CH_4	NiO	n.a.
Xi'an Jiaotong University, China	10	Interconnected Pressurised CFB-BFB	Coke oven gas	Fe_2O_3/CuO	15
ALSTOM Power Boilers, France	15	Interconnected CFB-BFB	n.g.	NiO	100
Korean Institute of Energy Research, KIER, Korea	50	Interconnected CFB-BFB (KIER-1) BFB-BFB (KIER-2)	CH_4 CH_4, CO, H_2	NiO, CoO NiO, CoO	28 300
Technical University of Viena, Tuwien, Austria	120 (CLC) 140 (CLR)	DCFB	CH_4, CO, H_2 CH_4	NiO, ilmenite NiO	>90 20
Solid fuels					
Chamers University of Technology, Chalmers, Sweden	10	Interconnected CFB-BFB	Coal, petcoke	ilmenite	90
Southeast University, China	10	CFB-spouted bed	Coal, biomass	NiO, Fe_2O_3	130
Ohio State University (OSU) Ohio, USA	25	Interconnected Moving bed-Entrained bed	Coal	Fe_2O_3	n.a.
ALSTOM Windsor, Connecticut, USA	65	Interconnected CFB-CFB	Coal	$CaSO_4$	n.a.
Darmstadt University of Technology, TUD, Germany	1 MW_{th}	Interconnected CFB-CFB	Coal	ilmenite	Operational in 2011
ALSTOM Windsor, Connectict, USA	3 MW_{th}	Interconnected CFB-CFB	Coal	$CaSO_4$	Operational in 2011

[a] The operation time corresponds to the period with particle circulation at high temperature.

According to [Adanez 2012], most of the CLC pilot plants existing worldwide at the moment use two interconnected CFB reactors working at atmospheric pressure. Alternative reactor concepts for CLC have only been tested at lab-scale.

Whilst small scale tests of the CLC process have been undertaken, a key to success is the ability to fully combust the coal in the fuel reactor. Although high conversions have been achieved the goal of effectively complete combustion has not. A solution to this is still needed. Some advocate the use of oxygen carriers that release gaseous oxygen under fuel reactor conditions in the CLOU variant of the process, which is discussed later. Two effects preventing complete combustion of coal in a fluidised bed reactor need to be addressed. The first is the tendency for volatiles released from the coal in the well mixed reactor to exit with the combustion gases before they have had enough contact time to oxidise. This can be worked around by installing an oxy-combustion polishing step, although this reduces efficiency because of the parasitic energy needed to produce the oxygen required. The other is that the heavier char needs a long residence time and in a well mixed reactor unburnt material circulates to the air reactor affecting the capture efficiency. Initial approaches have involved designs for staging the fuel reactor by inserting narrow sections so that it behaves less like a CSTR (continuous stirred tank reactor). Because of these issues the technology readiness level is assessed as still being at TRL-2.

[DOE/NETL 2013] contains a brief overview of the CLC projects supported by the US Department of Energy's (DOE) National Energy Technology Laboratory (NETL) that were completed in 2012. NETL considers CLC a "transformational" technology with the potential to meet programme cost and performance goals and be ready for demonstration-scale testing after 2030. The overview identifies the following four areas that need further R&D: (1) oxygen carrier characteristics, (2) solids circulation strategy, (3) reactor design, and (4) overall system and process design.

Generally, for CLC to be a viable option for reducing CO_2 emissions further development is necessary with regards to large scale CLC operation and conversion/retrofitting of existing facilities.

6.9. Chemical looping gasification (CLG)

Several gasification technologies for solid fuels exist that are suitable for combination with CLC. This section provides a brief description of the technologies that have been recently discussed in the literature, especially in [Adanez 2012].

6.9.1. In-situ gasification CLC (iG-CLC)

In-situ gasification CLC (iG-CLC) means gasification of a solid fuel by H_2O or CO_2 supplied as fluidization agent, i.e. direct feeding of the solid fuel to the fuel reactor. Figure 61 shows a scheme of this process. When CO_2 is the agent, the process can avoid the energy required for steam production. The net chemical reaction is the same as in usual combustion with the same combustion enthalpy.

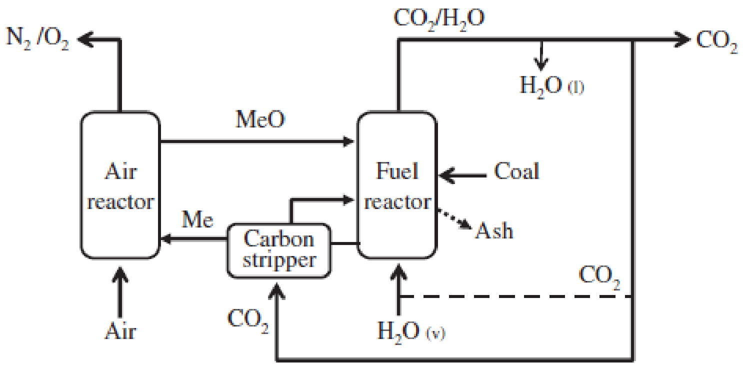


Figure 61 Scheme of the iG-CLC process [Adanez 2012]

[Shen 2009] evaluated biomass as a solid fuel in a continuous 10 kW$_{th}$ CLC combustor. However, they found a low reactivity of the oxygen carrier particles used due to sintering.

6.9.1.1. Performance and cost

Initial calculations indicate that the iG-CLC process has the potential to obtain higher power efficiencies and lower costs than other evaluated technologies, with a net efficiency of the process of about 41-42% [Fillman 2010]. Pressurisation of the process is an option to further increase the energy efficiency. According to [Adanez 2012], concepts using two interconnected fluidized-bed reactors are prevalent in the works demonstrating the iG-CLC technology.

6.9.1.2. Current status, technology readiness level and development requirements

This technology is still at the conceptual stage and is assessed at TRL-1.

[Adanez, 2012] also mentions the following key factors for the development of this process: (a) combustion efficiency in the fuel-reactor; (b) efficiency of char separation in the carbon stripper; and (c) separation of ash. The authors further discuss that it could be difficult to reach complete gas conversion with solid fuels even when using highly reactive oxygen carrier materials or high solids inventory. The unburnt components are another issue that needs to be addressed. Finally, mixing of the ash and oxygen carrier could have negative effects on performance of the oxygen carrier, such as loss in reactivity or agglomeration.

6.9.2. Chemical looping with oxygen uncoupling (CLOU)

In chemical looping with oxygen uncoupling (CLOU) a solid fuel is burned with gaseous oxygen released by the oxygen carrier in the fuel reactor. This avoids the low reactivity of the char gasification stage in the iG-CLC process. For comparison, Figure 62 provides the mechanisms of the different CLG technologies discussed in this section.

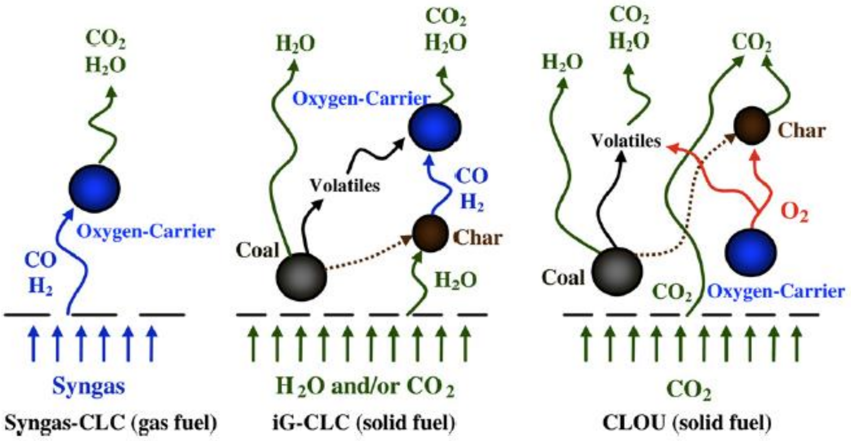


Figure 62 Mechanisms of the different CLG technologies [Adanez 2012]

6.9.2.1. *Performance and cost*

[Adanez 2012] contains a detailed discussion of CLOU and the authors mention that the lower amount of oxygen carrier material needed in the system will reduce the reactor size and associated costs. The fluidization gas can be recycled CO_2, which reduces the steam duty of the plant and the corresponding energy.

6.9.2.2. *Current status, technology readiness level and development requirements*

[Mattisson 2009] identified three suitable metal oxide systems for application in CLOU: CuO/Cu_2O, Mn_2O_3/Mn_3O_4, and Co_3O_4/CoO. The proof of concept of the CLOU process with coal was demonstrated in a 1,500 W_{th} unit located at ICB-CSIC consisting of two interconnected fluidized-bed reactors [Adanez-Rubio 2011].

This technology is very similar to the basic CLC except that a different type of oxygen carrier is required. A formulation for a viable system can only be made when solutions to the coal conversion efficiency have been satisfactorily addressed. While much of the large scale hardware needed is well developed, this particular application is, as for CLC, currently assessed to be at TRL-1.

[Adanez 2010] argue that the high temperature dependency of the O_2 concentration in the CLOU process makes the thermal integration between fuel reactor and air-reactor a key aspect in the development of the technology. A drawback of this technology compared to normal CLC for solid fuels, which uses natural ores as oxygen carriers, is the cost of the oxygen carrier. This higher cost must be compensated for with a very high carrier lifetime, a high and stable reactivity, and a high resistance towards ash fouling [Adanez 2012].

6.9.3. *Syngas-CLC*

[Adanez 2012] describes syngas-CLC as coal gasification with subsequent introduction of the syngas produced into the CLC system. The benefits of using natural gas as fuel apply to this process as well. Figure 63 shows the layout of the syngas-CLC process.

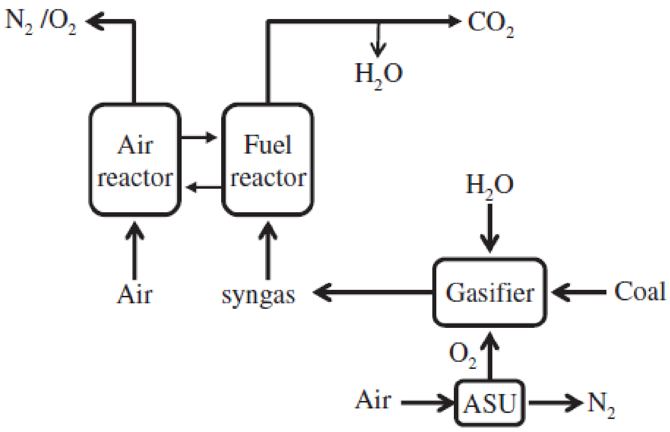


Figure 63 Schematic layout of the syngas-CLC process [Adanez 2012]

The following two processes are syngas-CLC technologies.

6.9.4. CLC in coal-based IGCC (ICLC-CC)

CLC can be integrated in a coal-based IGCC (ICLC-CC) power plant, instead of the conventional approach of a WGS reaction with subsequent CO_2 capture in a physical absorption process like Selexol or Rectisol. Figure 62 illustrates the layout of the process, where cleaned syngas from the gasifier is combusted in a CLC system. The products from the CLC reactor are separate high-temperature streams of O_2-depleted air and flue gas (CO_2 and H_2O), which can be used in a combined cycle power plant to generate electricity.

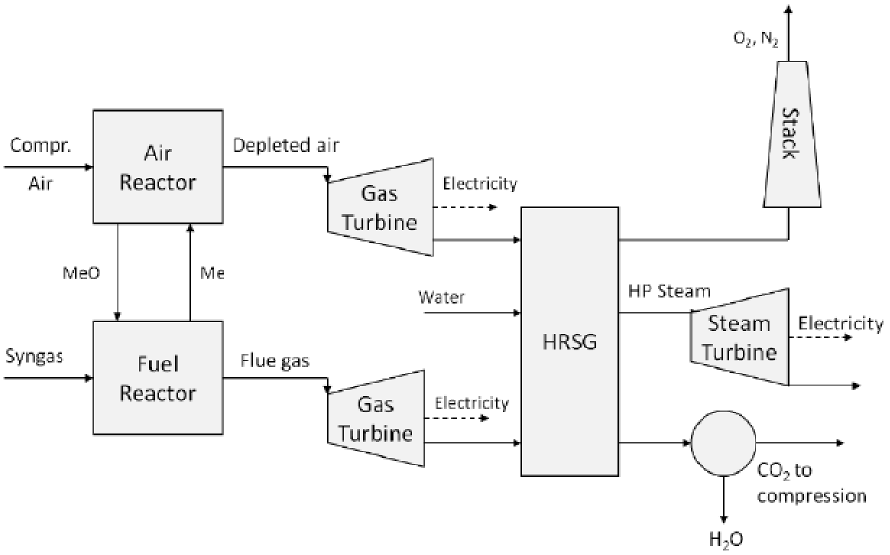


Figure 62 CLC combined cycle power plant using syngas as fuel [Mantripragada 2013]

6.9.4.1. Performance and cost (ICLC-CC)

[Xiang 2008] claims that integrating coal gasification, CLC and gas turbine combined cycle would have similar efficiencies as a system with conventional IGCC application but no CO_2 capture. [Jin 2008] reports an additional gain of 5-10%-points compared to conventional IGCC with CO_2 recovery.

[Mantripragada 2013] investigated performance and costs of this ICLC-CC process. The authors report a CLC system efficiency of 57.7% (based on higher heating value (HHV)) and an IGCC net efficiency of 38.9% (based on HHV) at a CO_2 capture rate of almost 100%. They found the COE to be ~90 US$/MWh and the plant capital cost to be close to 3040 US$/kW-net, with the CO_2 capture part amounting to more than 10% of the costs. Since ICLC-CC is a new technology, the authors assumed high contingency costs (about 50% of the direct cost) for the estimation.

The reported efficiency is exceptional as it is close to that of a baseline plant at 39.3% (HHV) This level of performance is clearly interesting despite the high estimate for the capital costs. Reasons for this high efficiency are probably related mainly to the fact that all of the mass flows of pressurised gases, both depleted air and burned fuel, are able to pass through the gas turbines. The temperatures of the outlets of the reactors and hence the top inlet temperatures of the turbines is limited to that of the two reactors. The paper suggests that the results are based on reactor temperatures of 1100°C and that this is anyway limited to maximum 1200°C because of melting point of suitable oxygen carriers. The paper suggests that the conventional IGCC process used in comparison was using an inlet temperature for the gas turbine of around 1350°C. Without doing detailed calculations it is difficult to fully assess the reasons for such high efficiency when the turbine inlet temperatures are so low. The lower turbine inlet temperature is expected to reduce overall efficiency by about 2.5%, even if the capture process consumed no energy, whereas a difference of only 0.4% is reported.

6.9.4.2. Current status, technology readiness level and development requirements

This technology is at the conceptual stage, although it is based on principles that have been researched. The technology readiness level is assessed as TRL-1.

[Adanez 2012] concludes that the ICLC-CC process remains a challenge due to the use of interconnected pressurized CFB reactors.

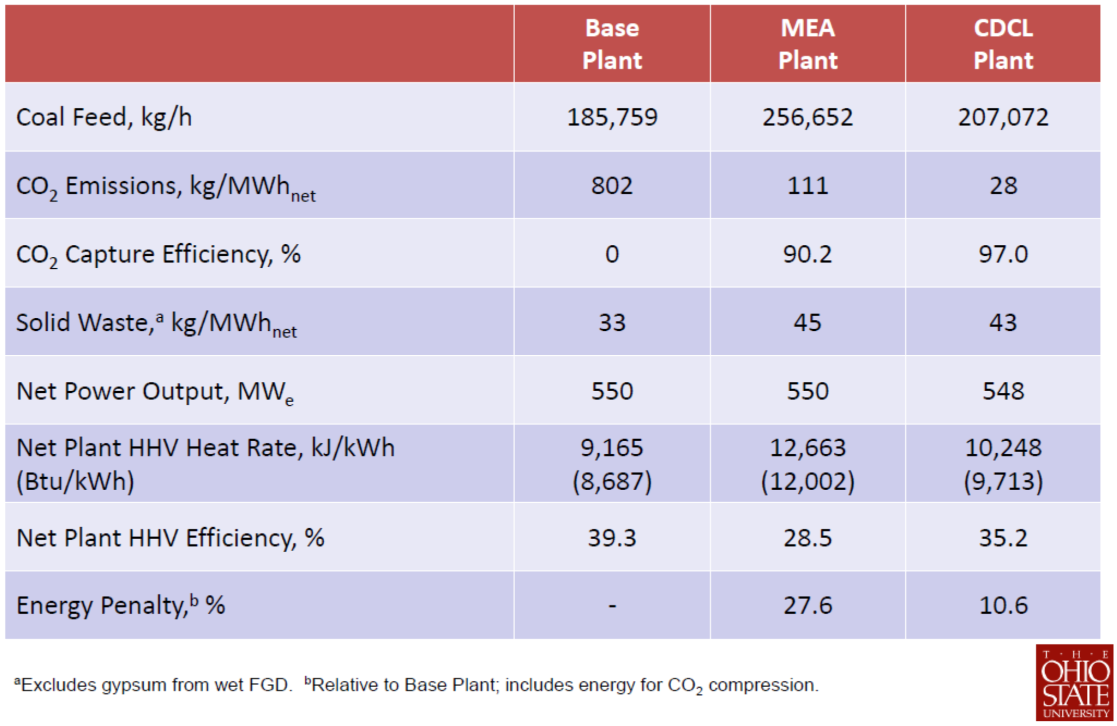
6.9.4.3. Coal-direct chemical looping (CDCL)

Ohio State University (OSU) is developing an iron oxide (Fe_2O_3)-based syngas chemical looping process for retrofit on existing coal-fired power plants with support by NETL. The CDCL system consists of a moving-bed fuel reactor and an entrained-flow combustor and is a versatile technology that can produce power, syngas or H_2, while offering fuel flexibility.

6.9.4.4. Performance and cost (CDLC)

The CDCL process has the potential to meet DOE’s goal of > 90% CO_2 capture at no more than a 35% increase in LCOE. Table 15 and Table 16 show techno-economic performance figures from an OSU simulation. CDCL increases the first-year COE by 33% compared to the base plant, whereas an MEA process would lead to a 71% increase [DOE/NETL 2013, Bayham 2013].

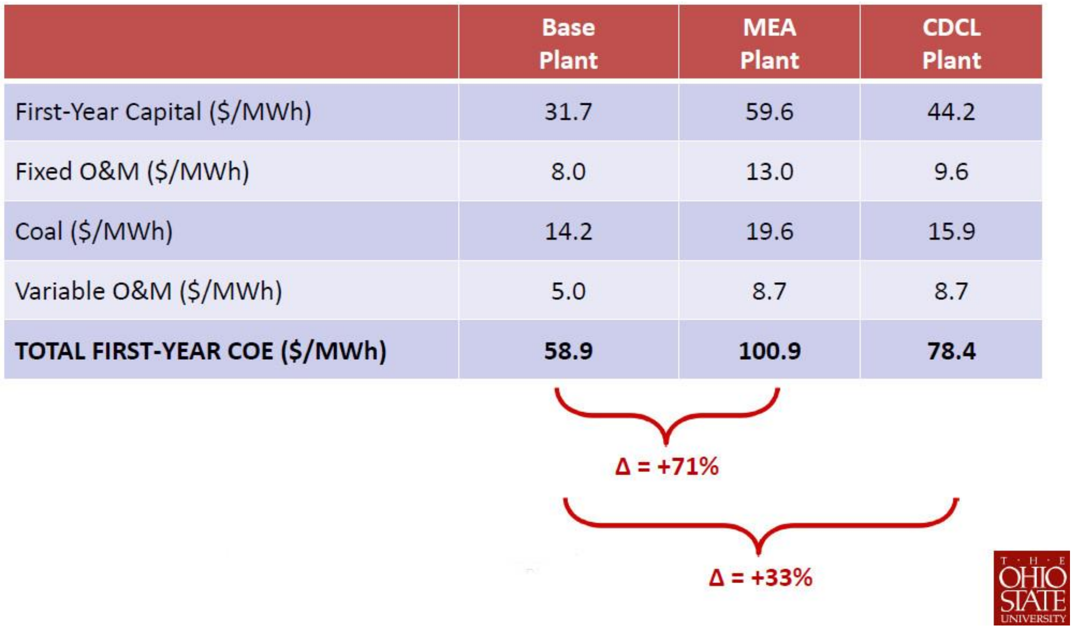
Table 15 Aspen Plus modelling results for CDCL process [Bayham 2013]



	Base Plant	MEA Plant	CDCL Plant
Coal Feed, kg/h	185,759	256,652	207,072
CO_2 Emissions, kg/MWh_{net}	802	111	28
CO_2 Capture Efficiency, %	0	90.2	97.0
Solid Waste,[a] kg/MWh_{net}	33	45	43
Net Power Output, MW_e	550	550	548
Net Plant HHV Heat Rate, kJ/kWh (Btu/kWh)	9,165 (8,687)	12,663 (12,002)	10,248 (9,713)
Net Plant HHV Efficiency, %	39.3	28.5	35.2
Energy Penalty,[b] %	-	27.6	10.6

[a]Excludes gypsum from wet FGD. [b]Relative to Base Plant; includes energy for CO_2 compression.

Table 16 First-year COE for CDCL process [Bayham 2013]



	Base Plant	MEA Plant	CDCL Plant
First-Year Capital ($/MWh)	31.7	59.6	44.2
Fixed O&M ($/MWh)	8.0	13.0	9.6
Coal ($/MWh)	14.2	19.6	15.9
Variable O&M ($/MWh)	5.0	8.7	8.7
TOTAL FIRST-YEAR COE ($/MWh)	**58.9**	**100.9**	**78.4**

Δ = +71%

Δ = +33%

The costs reported give an indication of the potential to reduce the increase in COE. However, the level of accuracy for the cost estimates for the fluidised bed systems will be less than for those for baseline facilities using conventional capture. At this stage it would appear that there is potential to halve the cost increase using this type of process. The reported plant performance suggests an energy consumption for capture of just 0.52 GJ/tonne abated.

6.9.4.5. Current status, technology readiness level and development requirements

OSU achieved > 800 hours of operation (incl. 200 hours of continuous operation) in 25 kW_{th} sub-pilot scale with nearly 100% CO_2 purity and a steady fuel conversion greater than 95%.

This technology is still at the conceptual stage, although it is based on principles that have been researched. The technology readiness level is assessed as TRL-1.

The Babcock and Wilcox Power Generation Group, Inc. (B&W) will validate the iron-based CDCL process and evaluate its potential as a cost-effective CO_2 capture technology for electric power generation [DOE/NETL 2013].

6.9.5. Chemical looping reforming (CLR) for H_2 production

Conventional CO_2 capture technology integrated with H_2 production is available today but usually only at high cost. The CACHET project [Beavis 2009] aimed to develop innovative technologies to reduce the cost of CO_2 capture whilst simultaneously producing H_2. The project evaluated two reforming technologies: (a) steam reforming integrated with chemical looping combustion (SR-CLC), and (b) autothermal chemical looping reforming (a-CLR). The SR-CLC process avoids the need of any CO_2 capture step, whereas the a-CLR process avoids the ASU required in conventional autothermal reforming.

The following section describe SR-CLC and a-CLR in more detail.

6.9.6. Steam reforming (SR-CLC)

[Adanez 2012] describes the SR-CLC process, which avoids the need of any CO_2 capture step from the exhaust gases produced in the heating of the reformer tubes. Figure 65 provides a scheme of the process. SR-CLC converts steam and hydrocarbons into syngas by conventional catalytic reforming. The main difference with respect to conventional steam reforming is that the CLC system provides the heat for the endothermic reforming reactions and CO_2 capture.

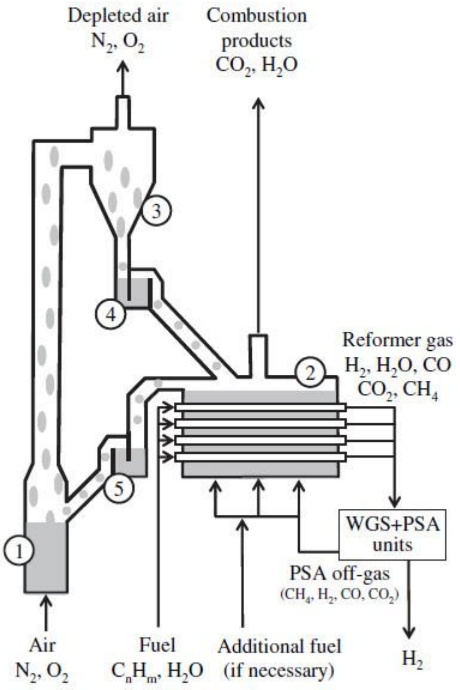


Figure 65 Scheme of SR-CLC process, (1) air reactor, (2) fuel reactor, (3) cyclone, (4) + (5) loop seals [Adanez 2012]

[Ortiz 2010] analysed the behaviour of several Fe-based materials (incl. synthetic materials and waste products) as oxygen carriers in a continuous 500 W_{th} unit.

6.9.6.1. Performance and cost

An integration of SR-CLC with WGS and pressure swing adsorption (PSA) can provide almost 100% CO_2 capture without any extra penalty in efficiency. [Adanez 2012] assumes the working conditions and the oxygen carriers used in SR-CLC could be the same as those for conventional CLC.

[Ortiz 2010] found that the addition of a Ni-based oxygen-carrier to Fe-based oxygen carrier materials had a positive effect on the combustion efficiency.

6.9.7. Autothermal reforming (a-CLR)

The a-CLR process utilizes the same basic principles as CLC, the main difference being that the desired product is H_2 and not heat. [Adanez 2012] contains an overview of the process (for a schematic layout please refer to Figure 66). Key advantages are the avoidance of the ASU as compared to conventional auto-thermal reforming, the inherent CO_2 capture and that there is no need for an external heat source.

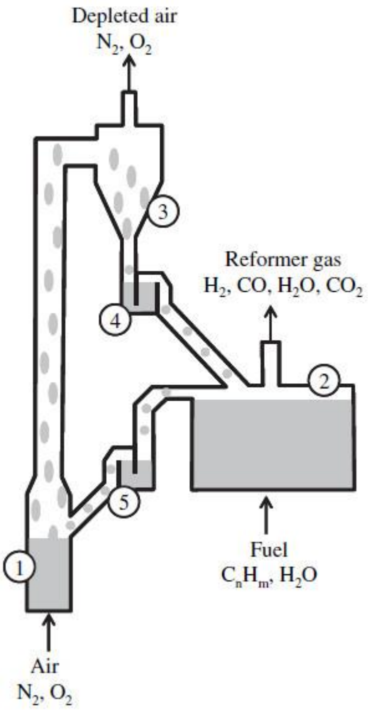


Figure 66 Scheme of a-CLR process, (1) air reactor, (2) fuel reactor, (3) cyclone, (4) + (5) loop seals [Adanez 2012]

[Pröll 2010] demonstrated the a-CLR process in a 140 kW_{th} dual CFB installation.

6.9.7.1. Performance and cost

[Ortiz 2011] reports that the H_2 yield in this process can reach 2.7 $molH_2/molCH_4$. [Ortiz 2010] studied the performance of a pressurized a-CLR system and observed high CH_4 conversion (> 98%). The oxygen carriers did not show any agglomeration or defluidisation problems and attrition was negligible.

[Ryden 2008] concluded that pressurized CLR has the potential to achieve efficiencies about 5% higher because pressurized systems reduce the energy penalty for H_2 compression.

6.9.7.2. Current tatus, technology readiness level and development requirements

The reforming processes proposed above differ only in that one uses CLC simply as a heat source whilst the other uses the oxygen carrier to provide oxygen to a partial oxidation reaction. The former has much more complex equipment requirements in particular the engineering of the reformer tubes inside the fuel reactor. Thus the indirect heated approach is at the stage of an initial concept. The technology readiness level is assessed as TRL-1. The direct process does not require such complex engineering as it is based on a coupled CFB system which has been tested in numerous similar applications. A single test has been performed and more extensive work would be needed to validate the process. The technology readiness level is assessed as TRL-3.

As pressurized CFB operation is not yet a standard technology, more research and development effort will be necessary. A key issue for the CLR technology development is the selection of an oxygen carrier with suitable properties [Adanez 2012]:

- Enough reactivity through cycles to reduce solids inventory
- High resistance to attrition to minimize losses of elutriated solids
- Complete fuel conversion to CO and H_2
- Negligible carbon deposition, as this would release CO_2 in the air-reactor
- Good fluidization properties (no presence of agglomeration)
- Oxygen carrier with simple preparation method to reduce costs

6.10. Limestone chemical looping (LCL): a hybrid process

Alstom is developing a hybrid combustion-gasification chemical looping process that uses $CaSO_4$ as oxygen carrier. Figure 67 shows the principle of the process that couples a $CaCO_3$/CaO cycle with a $CaSO_4$/CaS cycle. The process has three options, i.e. it can produce heat, syngas or H_2 [Abdullaly 2012]:

1) Chemical looping combustion: product gas is CO_2, heat produces steam for power
2) Chemical looping gasification: product gas is syngas, no inherent CO_2 capture
3) Hydrogen production: product gas is H_2, calciner off-gas is CO_2

According to [Adanez 2012], a drawback for the use of $CaSO_4$ is the possible formation of CaO and SO_2. CaO can eliminate the oxygen transport capacity of $CaSO_4$, thus requiring the addition of fresh carrier. To minimise sulphur release (either as SO_2 or H_2S), Alstom's process works at temperatures below 980°C in the fuel reactor.

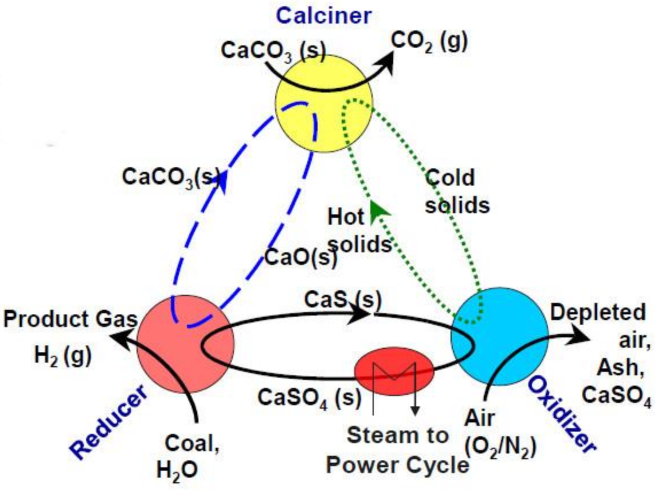


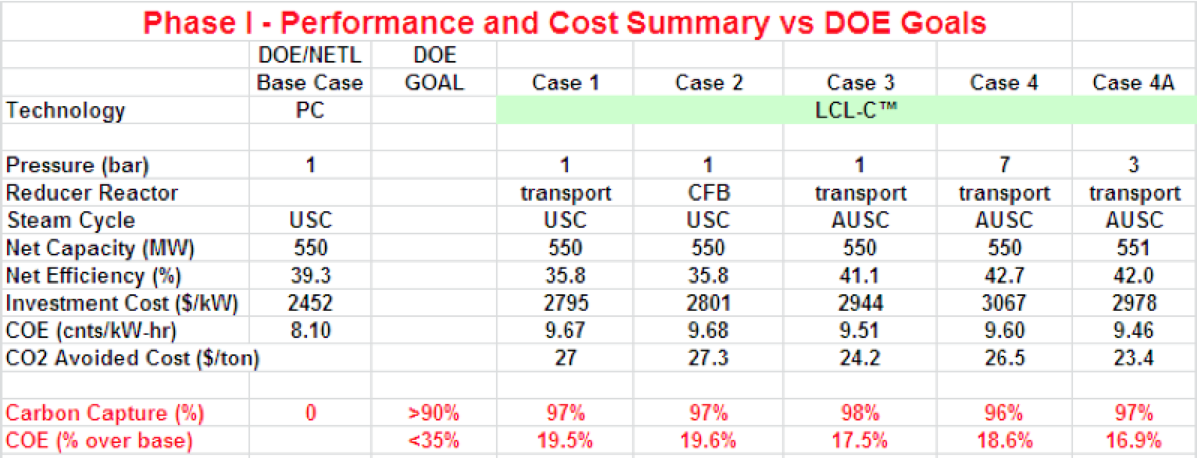
Figure 67 Alstom's LCL process [Abdullaly 2012]

6.10.1. Performance and cost

[Marion 2013] presents performance and economic data for the LCL process compared to conventional oxy-combustion. The CO_2 capture cost was 79.3 US$/t$CO_2$ for the oxy-combustion case and 27.0 US$/t$CO_2$ for the LCL case. [Marion 2013] concluded that LCL has the potential to be one of the lowest cost technologies for CCS in coal-fired systems.

Recently updated information released by Alstom [Alstom 2014] confirms this cost as shown in the table below.

Table 17 LCL performance and costs [Alstom 2014]



Phase I - Performance and Cost Summary vs DOE Goals

	DOE/NETL Base Case	DOE GOAL	Case 1	Case 2	Case 3	Case 4	Case 4A
Technology	PC		LCL-C™				
Pressure (bar)	1		1	1	1	7	3
Reducer Reactor			transport	CFB	transport	transport	transport
Steam Cycle	USC		USC	USC	AUSC	AUSC	AUSC
Net Capacity (MW)	550		550	550	550	550	551
Net Efficiency (%)	39.3		35.8	35.8	41.1	42.7	42.0
Investment Cost ($/kW)	2452		2795	2801	2944	3067	2978
COE (cnts/kW-hr)	8.10		9.67	9.68	9.51	9.60	9.46
CO2 Avoided Cost ($/ton)			27	27.3	24.2	26.5	23.4
Carbon Capture (%)	0	>90%	97%	97%	98%	96%	97%
COE (% over base)		<35%	19.5%	19.6%	17.5%	18.6%	16.9%

These figures suggest that the LCOE will increase by just under 20% compared to baseline post-combustion. This compares with assessments for post- and oxy-combustion baselines with capture of 100% and 80% increases in LCOE. This represents a very large claimed reduction. That said it has to be realised that full calibration of estimates requires detailed work using a consistent set of parameters.

6.10.2. Current status, technology readiness level and development requirements

Alstom scaled-up the LCL process from a 65 kW_{th} pilot, which was successfully demonstrated in an earlier project (DOE project NT41866), to a 3 MW_{th} prototype facility that was operational in 2010 and 2011 (DOE project DE-NT0005286). Alstom was able to operate the 3 MW_{th} prototype for 12 hours under autothermal conditions, using only coal as fuel and achieving 96% capture of CO_2 [DOE/NETL 2013, Marion 2013]. The 3 MW_{th} unit is currently undergoing modifications prior to a further testing programme. All tests so far have been in two reactor configuration for CLC.

The LCL technology has been tested in two reactor configuration with encouraging initial test results. The testing is due to resume in a modified equipment. The basic concept of the two coupled reactors has been successfully demonstrated in other locations and the main difference in Alstom’s process is the different oxygen carrier. The performance and stability of this are critical to successful development. The next phase of testing is aimed at resolving a number of issues identified so far, which, if successful, will raise the readiness level. The technology readiness level is assessed as TRL-4.

In addition, the formation of CaO and SO_2 need further investigation and clarification

7. CCS Development in Non-Power Industries

Non-power energy intensive industries are in general not very keen on immediate deployment of CCS due to its impact on their market competitiveness but several of these industries have investigated what are the options available to them to capture the CO_2 emissions from their plants. This report will only review the technologies currently evaluated by the different energy intensive industries and highlight the different directions taken in developing CCS in their industries.

7.1. Iron and Steel Industry

Steel is produced either from virgin ore or from scrap. Currently, there are three leading groups of technologies that produce steel from virgin ore. These include: (a.) Blast Furnace – Basic Oxygen Furnace (BF-BOF) route, (b.) Smelting Reduction – Basic Oxygen Furnace (SR-BOF) route, and (c.) Direct Reduction – Electric Arc Furnace (DRI-EAF) route.

Some of the key features of an integrated steel mill via the BF-BOF route are:

- CO_2 is emitted from various point sources within the site. Nearly 90% of the CO_2 is emitted from the operation of the coke production, sinter production, lime kilns, BF's hot stoves, on-site power plant and finishing mills.
- CO_2 emissions profiles vary from site to site.
- Most of the CO_2 emitted is from the combustion of the by-product fuel gas derived from the blast furnace, coke ovens and basic oxygen furnace.

For the steel production via the BF-BOF route, the hot metal production (i.e. iron making process / blast furnaces) is the most carbon intensive process. This is responsible for up to 80-90% of the CO_2 emissions of the whole steel mill. However, the direct CO_2 emission attributed to this process is only ~20-25% of the total emissions (i.e. predominantly the CO_2 emitted from the flue gases of the hot stoves). The other CO_2 is emitted in other processes by burning of the blast furnace gas as fuel.

The global steel industry has been very active in developing CCS in the past decade. There are three major RD&D programmes on-going in Europe, Japan and South Korea. The focus of their work is the capture of CO_2 from the blast furnace gas.

It should be noted that the steel industry has concluded that the capture of CO_2 from various flue gases within their sites is not economically viable. They have concluded that to deploy CCS within their industry will require new development in the iron making process that would also increase efficiency.

ULCOS Programme (Europe)

The ULCOS Programme [van der Stel, 2013a; Meijer and Zeilstra, 2011; Silkström, 2013; Birat, 2010; 2012] is Europe's leading programme in development of breakthrough technologies for the steel industry. Three out of the four technologies they have shortlisted would require CCS to reduce CO_2 emissions intensity by greater than 50% - these include:

- ULCOS BF – Oxygen Blown BF with Top Gas Recycle
- HISARNA
- ULCORED

a.) ULCOS BF

ULCOS BF or Oxygen-Blown BF with Top Gas Recycle [van der Stel, 2013a ; Birat, 2010] is a revamped version of the conventional blast furnace. CO_2 is separated from the top gas before it is recycled back into the blast furnace; whilst the captured CO_2 could be transported and stored. ULCOS has evaluated various technologies that could separate CO_2 from the top gas and these include:

- Pressure Swing Adsorption (PSA)
- Vacuum Pressure Swing Adsorption (VPSA)
- PSA or VPSA in combination with cryogenic separation
- Chemical Absorption

Component development for the ULCOS BF, i.e. tuyeres technology (gas injection), process gas heaters, etc. are currently being pursued. The future direction in the development of the ULCOS BF is to validate the coke reduction potential introduced by the top gas recycle. This could only be achieved in large scale demonstration plant.

b.) HISARNA

HISARNA [van der Stel, 2013a; Meijer and Zeilstra, 2011] is one of the smelting reduction technologies for hot metal production. This is a combination of three different technologies that include the cyclone converter furnace (CCF), HISMELT and screw feeder / coal pyrolysis.

The main driver of the HISARNA's development is the reward of reducing CO_2 emissions by eliminating the coke and sinter production processes. Without CO_2 capture, the HISARNA process could potentially achieve a reduction of at least 25% of the total emissions as compared to the best performing integrated steel mill using BF/BOF route. With CCS, this could achieve up to 80% CO_2 emissions reduction of the steel production.

Currently, the HISARNA is being tested in a pilot scale. Further tests will be needed to validate its reliability and engineering design for scale up. HISARNA technology is considered a high risk and high reward option for ULCOS. The future direction of this development would require demonstration of a scaled-up version of the HISARNA process; and ultimately to achieve a production capacity of at least 2 million tonnes of hot metal annually in order to compete against the economics of steel production based on the BF/BOF route.

c.) ULCORED

ULCORED [Knop et al, 2008; Silkström, 2013] is the development of a shaft based ore reduction process using H_2 rich syngas to produce DRI, and at the same time capturing greater than 50% of the CO_2 emitted from the process. Development of this technology includes both gas and coal based DRI production.

The production of the DRI using gas-based ULCORED involves a shaft reactor fed with lump ore or pellets and uses nearly pure oxygen to burn pre-heated fuel in a partial oxidation reactor (POX) to produce the H_2 rich syngas as the primary reducing gas. The process involves the use of a shift reactor to convert at least 90% of the CO in the cleaned off-gas from the shaft reactor to produce H_2 and CO_2. The CO_2 is then separated using VPSA or PSA. Most of the top gas from the PSA or VPSA is used as cooling medium of the DRI. This is generally mixed with natural gas to make up the fuel demand of the POX reactor. Some part of the top gas will be preheated in the shift reactor and mixed with the syngas produced by the POX. Finally, a minor part of the gas could be exported to the steelworks as by-product fuel to bleed out the nitrogen content.

The coal based DRI involves the use of coal gasification with water shift reactor. The H_2 rich syngas is then used as the primary reducing agent to the shaft reactor. CO_2 separation technologies for this process could be different to the gas based ULCORED (i.e. options for physical absorption are possible).

Some of the current development and key challenges of ULCORED are:

- Nearly every major component of the gas-based DRI reactor is in commercial operation (shaft reactor, shift reactor, PSA/VPSA and POX). However, integrating these components to produce the DRI and capture the CO_2 at the same time would require large scale demonstration to test its availability, reliability and the quality of its products (DRI and CO_2).
- Development of the pilot plant is an important element of the demonstration of ULCORED. This should provide the opportunity to establish and validate the different technical and economic parameters in the integration of the different components of ULCORED.
- To reduce investment cost, the scaling up of all the components could be an important element of consideration in the engineering of the ULCORED. For example, the largest POX reactor currently operating today using NG is producing ~200,000 Nm^3/h of syngas (plant operated by Linde). This means that at least two trains of POX reactor are necessary to meet the demand of a single train shaft reactor at today's capacity that could produce in the range of 2.0 to 2.5 Mt/y of DRI.
- Like any DRI usage in steel production, the major source of indirect CO_2 emissions is the electricity consumption during the melting of the DRI in the EAF. An additional feature of the development of the ULCORED process is the deployment of COMELT technology (an EAF using DC power) developed by Siemens VAI which improves the electricity consumption of melting DRI.

COURSE50 Programme (Japan)

The COURSE50 programme [Osame, 2011; Watakabe, 2013; JISF, 2013] is a consortium of Japanese steel and allied industries funded by NEDO with an objective to evaluate options to reduce GHG emissions from steel production.

The different technology options evaluated under COURSE50 include the following:

- Technologies that reduces CO_2 emissions from the blast furnace (i.e. technologies that reduce coke consumption of the BF)
    - Development of hydrogen injection technology to the BF and relevant control systems
    - Development of pre-reduction shaft reactor using hydrogen as the primary reducing agent and introduction of pre-reduced ore into the BF
    - Utilisation of CO rich gas from the CO_2 capture plant as a reductant for the BF and Pre-reduction shaft reactor.
- Technologies for CO_2 capture and storage (i.e. technologies that capture CO_2 from the BFG)
    - Development of chemical absorption technology
    - Development of physical adsorption technology
- Technologies that support COURSE50 Technologies
    - Improvement to coke ovens to produce coke that is optimum for hydrogen injection
    - Development of COG reformer to increase its hydrogen content (H_2 amplification)
    - Development of sensible heat recovery from steelmaking slag
    - Development of Kalina cycle power generation technology
    - Utilization of Phase Change Materials or PCM
    - Utilization of heat pumps

The future direction of the current development will be initially aimed at validating performance of each component and this should be followed by combining all technology development into a large scale demonstration.

a.) Technologies that reduce CO_2 emissions from the blast furnace

The cornerstone of this development is to enable the use of H_2 or H_2-rich gas as reducing agent in the blast furnace that could result in coke reduction. Key to this development includes (but is not limited to):

- Identification of the feed conditions of the pre-heated H_2/H_2-rich gas
- Quantification of the reducibility of the iron ore when using H_2/H_2-rich gas
- Combustion simulation at the tuyere raceway with high H_2/H_2-rich gas level
- Evaluation of the balances of the energy and CO_2 of the entire steel works

To support this development would require the development of high strength coke to maximise coke reduction when feeding with H_2/H_2 rich gas. This involves the development of high performance caking (HPC) additives. The role of the HPC involves the lowering of the softening and melting temperature of coking coal thus allowing these additives to fill in the pores within the coke resulting in increased coke strength index.

b.) CO$_2$ capture by Chemical Absorption or Physical Adsorption

The Japanese programme concluded that CCS is required to achieve drastic reduction of CO$_2$ emissions from steel production. In this area, chemical absorption [Watakabe, 2013; Osame, 2011] and physical adsorption [Saima et al, 2013; Osame, 2011] technologies are the main focus of development to capture CO$_2$ from blast furnace gas. Currently, pilot plants for both technologies have been demonstrated.

The chemical absorption technology involves the development of proprietary solvent to achieve better performance (i.e. heat of regeneration of 2 GJ/t CO$_2$ or better) for CO$_2$ capture ready for the large scale demonstration plant. The work involves the evaluation of the solvent properties using CAT-1 pilot plant, and the improvement of the chemical absorption process using the CAT-30 pilot plant.

The physical adsorption technology involves the use of PSA separating the CO$_2$ and CO/H$_2$ from the blast furnace gas in two stages. This involves the use of adsorbent based on zeolites. Their test aims to evaluate the performance of the adsorbent to achieve at least 80% recovery and 90% CO$_2$ purity.

To support the development of the CO$_2$ capture technologies, the programme also pursued the development of recovering unused waste heat from the steel mill. One of the primary candidates of this development is the recovery of heat from BF and BOF slag.

POSCO / RIST Programme (South Korea)

Development of CCS technology for the steel industry in South Korea is supported by the Korean Ministry of Knowledge with some contribution from the private sector. The main scope of work includes [Lee, 2013; Ahn, 2011]:

- Capture of CO$_2$ from the BFG.
- Recovery and utilisation of waste heat within the steelworks
- Utilisation of CO$_2$ and CO for other industrial users

The POSCO / RIST Programme has evaluated the use of aqueous ammonia (10%) process to remove the CO$_2$ from the BFG. The recovery and utilisation of waste heat is based on development of technology to recover heat from BF slag; whilst the CO$_2$ utilisation technology is based on reformation of COG to produce CO and H$_2$ to be recycled back into the blast furnace.

a.) Development of CO$_2$ Capture Technology Using Aqueous Ammonia Solution

The capture of CO$_2$ using aqueous ammonia process is based on chemical absorption process using 3 columns – absorber, stripper and NH$_3$ concentrator. They have tested this process in a pilot plant handling 1000 Nm^3/h BFG and have achieved >90% capture rate with CO$_2$ purity between 95-98% (v/v wet basis). It was reported that at 9% aqueous ammonia solution, the steam consumption for solvent regeneration is ~1.5 kg of steam/t CO$_2$ (i.e. energy consumption of ~3.0 GJ/t CO$_2$). The ammonia slip is considered minimal.

The future direction of research will involve the improvement of the chemical absorption process (i.e. use of additional lean NH_3 pumps for intermediate cooling) and the use of higher ammonia concentration. Future work is aimed at testing long term continuous operation to validate process reliability and basic engineering design for commercial scale demonstration.

b.) Development of Waste Heat Recovery Technology from BF Slag

The development of this technology under the South Korean programme has a similar direction to the Japanese Course50 programme. The basic aims of this development are the development of the dry granulation and fast cooling of BF slag to recover waste heat. The conceptual design of the process involves at least a heat recovery of 50% from the molten slag and a production unit with a capacity of 180 t BF slag/h.

c.) CO_2 Utilisation Technology

The utilisation of CO_2 within the steel mill is the primary driver for this technology development that will consequently reduce the CO_2 to be transported and stored or resolve the lack of CO_2 storage capacity in South Korea.

The main objective of this research area is to make use of the captured CO_2 as the reagent to reform the coke oven gas to produce CO/H_2 syngas. This syngas could be used as additional reductant in the blast furnace or the Finex process.

The future direction of this work is aimed at:

- Development of highly coking-resistant catalyst for the COG reforming
- Optimization of reaction condition, heat integration, and scale-up of the reactor

7.2. Cement Industry

Cement is a blend of clinkers and other cementitious materials. Clinkers are produced by heating limestone (calcium carbonate) with small quantities of other materials (such as clay) to 1450°C in a kiln. CO_2 emitted from the kiln is derived from the burning of fuel and from the decomposition of calcium carbonate (calcination process).

Currently, the cement industry has exploited to a great extent the reduction of CO_2 emissions by efficiency improvement, use of alternative fuel, and use of clinker substitutes. It has been recognised within the industry that to reduce drastically the CO_2 emissions, CCS would be required. Key stakeholders have identified the need to do pilot tests of CO_2 capture technologies to demonstrate and validate key technical viability as one of the requirements to enable CCS deployment in the future.

This section of the report provides a summary of the current CCS activities undertaken by the cement industry.

Post combustion capture and oxyfuel combustion are the CO_2 capture technologies which are most compatible with cement plants [IEAGHG, 2008, 2013]. Pre-combustion capture is at a disadvantage because it would not capture the CO_2 produced by mineral decomposition. Additionally, the use of gaseous fuel could also penalise the productivity of the cement kiln.

Table 18 shows the current status of the CO_2 capture technologies considered and their impact to the cement plant.

Table 18: Current status of Post- & Oxyfuel Combustion Technologies Applied to Cement Industry [Adapted from IEAGHG 2013]

	Oxyfuel Combustion	Post-Combustion CO_2 Capture (Solvent scrubbing)
Concept	Integrated concept	End of Pipe Technology
Development Status	Oxygen enrichment has been applied to cement kiln Oxyfuel combustion will require some R&D	Commercially available and applied in other industry Pilot testing applied to cement kiln initiated
Time Horizon for Commercial Application	Not before 2025	Not before 2020
CO_2 purity	CO_2 in the flue gas from combustion is ~85% (v/v dry basis) and purified in the CO_2 purification unit (CPU) Development of the CPU technologies in oxyfuel combustion for coal fired power plant should be adaptable	Delivered as high purity CO_2 (i.e. 90-99% v/v dry basis)
Applicability to Existing Plant	Retrofit is feasible and will require modification to the existing plant Space requirement for the ASU & CPU Existing plant structure has to allow for oxyfuel combustion technology infrastructure	Retrofitting is possible without redesigning of the kiln High space requirement for capture plant and power generation
Energy Requirement	High electricity demand for ASU and CPU resulting in doubling of power demand per tonne of clinker produced. Thermal energy demand could be reduced	High energy consumption for solvent regeneration resulting in doubling of electrical and thermal demand per tonne of clinker produced.
CO_2 Avoidance Cost	40 – 50€ / t CO_2.	65 -110€ / t CO_2

Other technologies have been also considered. These include the following:

- Calcium looping
- Membranes
- Adsorption Technologies

Some of these technologies have pilot plants built and validation tests on-going. Most of these technologies is expected to have similar development pathways to technologies applied to the power generation industry.

Below is the list of post-combustion capture pilot facilities applied to the cement industry worldwide:

- Norcem, Brevik, Norway: Test centre offering the possibility to conduct several small scale or pilot trials of post combustion capture using cement plant flue gas (2013-2017). Companies involved in this project include Aker Solutions (amine scrubbing), RTI (dry adsorption with specialized polymers), KEMA, Yodfat and NTNU (membranes) and Alstom (calcium looing).

- ITRI/Taiwan Cement Corp.: Pilot plant capturing 1 tonne CO_2/h from a cement plant and a power plant using a calcium looping process, commissioned June 2013.

- Skyonic Corp.: Plant under construction, capable of capturing 83,000t CO_2/y from a cement plant in Texas, using the “SkyMine” process. In this process salt and water are electrolyzed to produce hydrogen and chlorine gases and sodium hydroxide solution, which is reacted with CO_2 in flue gas to produce sodium bicarbonate, which can be sold on the market. Other combinations of chemicals can also be produced

A pilot plant trial of oxy-combustion in a cement plant calciner with a capacity of 2-3t/h of feedstock has been undertaken by FLSmidth, Air Liquide and Lafarge at Dania, Denmark [Gimenez, 2014]

In the near term, the direction of the RD&D will focus on deploying pilot scale facilities to validate the technical viability of CO_2 capture technologies applied to the cement industry. This is an important step necessary toward large scale demonstration.

7.3. Oil Refining

Oil refining is the processing of crude oil to produce petroleum products such as LPG, naphtha, gasoline, kerosene, diesel, gas oil and bottom products (bunker fuel, bitumen, etc.). Refineries are complex sites that are highly integrated and characterised by diverse process configurations. CO_2 emissions vary from site to site depending on refinery complexity and fuel types used. Figure 68 shows an example illustrating the breakdown of CO_2 emissions by process from a hydroskimming (simple) refinery and a more complex conversion refinery.

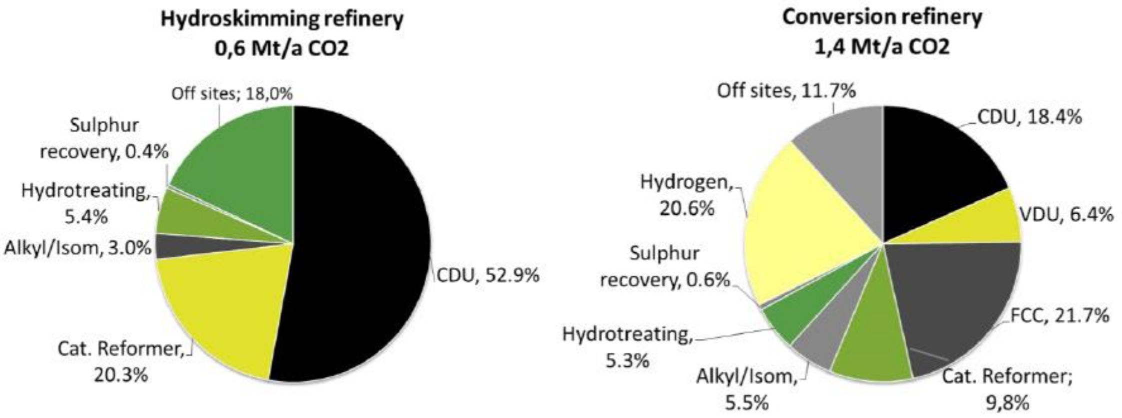


Figure 68: Refinery CO_2 emissions breakdown by process (%m/m) from hydroskimming (simple) and conversion refinery with capacity of 150,000 bbl/d (CONCAWE, 2011)

A refinery emits between 0.2 and 0.4 tonne CO_2 per tonne of crude processed for simple to medium/high conversion refineries, and can reach between 0.7 and 0.8 tonne CO_2 per tonne of crude processed if delayed cokers or residue gasifiers are included. Refineries usually have a small number of large emission sources and a large number of smaller, dispersed, low concentration sources.

Table 19 presents the top 4 processes within the refinery complex where deployment of CO_2 capture would be most likely.

Table 19: Potential Processes Suitable for CO_2 Capture in an Oil Refinery (CONCAWE, 2011)

Process	Description	% of Total Refinery Emissions	CO_2 Concentration in the Stream
Hydrogen Production Unit	Requirement for many processes. (i.e. product upgrading and desulphurisation)	5-20%	95-99% (chemical absorption) 40-70% (PSA) 4-8% (reformer flue gas)
Fluid catalytic cracking	This is the largest single source of CO_2 emissions among the different oil refining processes	20-55%	10-20%
Process Heaters and Boilers	This consists of the heat and steam production where emissions are at various point sources	30-60%	8-10%
Utilities (i.e. CHP, Power Plant etc)	Electricity/steam use at refinery	20-50%	3-12%

Capture from Hydrogen Production Unit

Most common hydrogen production units are based on steam methane reformer (SMR). Partial oxidation (POX) and petcoke gasifiers are also commonly used if a refinery has significant petcoke production. The hydrogen production unit can contribute a significant proportion of the overall CO_2 footprint of many refineries and is a major single-point CO_2 emission source. Typically, the vent from SMR hydrogen production has a high CO_2 partial pressure.

Foster Wheeler [Ferguson and Stockle, 2012] has reviewed 4 different technology options for CO_2 capture in SMR for different overall CO_2 capture ratios. This includes the use of PSA, post-combustion capture, non-PSA pre-combustion capture and hybrid post- and pre-combustion capture option.

The capture of CO_2 from the hydrogen production unit can be considered a low hanging fruit for CCS demonstration applied to the oil refining sector. Three leading large scale CCS demo projects in the world (i.e. Port Arthur Project – USA; Quest Project – Canada; and Tomakomai Project - Japan) are hydrogen production unit based on SMR technology. Port Arthur and Tomakomai Projects are directly connected to oil refineries; and the Quest Project is connected to an oil sand upgrader.

Capture from Fluid Catalytic Cracker (FCC)

The fluid catalytic cracker (FCC) is often the single largest source of CO_2 among the different oil refining processes. The emissions from FCCs are process related rather than combustion related, and associated with the regeneration of a catalyst used in the process. Depending on the process selection and quality of feedstock, the CO_2 concentration in the flue gas can range from 10% to 20%.

The use of post-combustion technology, such as amine or chilled ammonia CO_2 capture, has been evaluated at Test Centre Mongstad. Emerging technologies such as oxyfiring of the FCC is also currently being evaluated at a pilot plant by Petrobras in Brazil [Mello et. al., 2009].

Capture of CO_2 from Process Heaters, Boilers and Utilities

Refineries employ numerous fired heaters (or process heaters) of different sizes and capacity throughout the facility. These heaters could have capacities ranging between 2 to 250MW, and a typical refinery could have between 20 and 30 different inter-connected processes around the site. Most often, these process heaters use different types of fuel that are available on-site thus producing flue gas with wide ranging CO_2 compositions. However, it should be noted that it is not unusual for some of these emission sources to be connected to a common stack. Combined stacks can have CO_2 concentrations as high as 15%, emitting up to 1.2 Mt/CO_2 per year.

Emissions from the utilities of oil refineries are typically related to the emissions of the captive power plants, CHPs or boilers. Refineries require a large amount of steam and electricity to meet the energy demand of the different processes. Steam is provided on site either by boilers or CHPs. In order to increase efficiency, most refineries nowadays use cogeneration of heat and power. In some cases, natural gas is used as fuel for the industrial gas turbines producing electricity, while waste heat is recovered and utilised to produce steam.

These processes closely mirror those used in the power generation sector, which therefore implies that opportunities for applying CO_2 capture technologies in the utilities and boilers of the refineries will follow the CO_2 capture technology development of the power generation sector. Several works has been reported evaluating the use of post-, pre- and oxyfuel capture technologies [CO_2 capture project – CCP; van Straelen et. al. 2010; Jamaluddin et. al., 2012; Weydahl, et. al., 2013].

Future Direction of CO_2 Capture Deployment in an Integrated Oil Refinery

It is expected that there will be a varying degree of deployment of CCS applied to integrated oil refineries over time.

CO_2 capture technologies being developed include but are not limited to:

- Post-Combustion with CO_2 Capture
- Oxyfuel Combustion with CO_2 Capture
- Pre-Combustion with CO_2 Capture.

Other technologies such chemical looping, physical adsorption and membranes are also being considered.

CCS applied to hydrogen production units are currently demonstrated in larger scale at various sites worldwide. This is considered as the lowest cost among all the possibilities within an integrated oil refinery.

Development of CO_2 Capture for process heaters, boilers, and utilities is expected to follow the pathway of development of CO_2 capture in the power generation sector.

A pilot plant of Oxy-FCC has been evaluated and test is currently on-going. Basic engineering and scale up of the process will be necessary to move this forward to demonstration.

8. Conclusions

This study has collected together a considerable body of information on emerging capture technologies and has critically examined the claims for improved performance. It has resulted in identification of a number of promising new capture technologies. It has also provided insights into the cost and thermodynamic limitations which apply to many of the CO_2 capture processes and has identified those target areas likely to yield the greatest cost improvements. An extensive list of references has been generated, although those which are listed in the report represent only some of those which are available in the literature. These prime references provide a good lead to this more extensive information.

The study has highlighted difficulties and pitfalls that exist when attempting to make cost comparisons between diverse technologies. It proposes a procedure which might be developed to simplify cost estimation for comparative purposes making use of information generated by some of the excellent and detailed cost studies of benchmark capture processes.

A number of other key findings are listed below.

- Costs of CO_2 capture technologies are expected to decrease after they have become established at a commercial scale, due to learning-by-doing and incremental technology improvements, although costs of new technologies tend to increase during the development phase

- Further reductions in the costs of CO_2 capture may be achieved by use of new technologies. Estimating the cost reductions that could be achieved by new technologies is subject to large uncertainties. Assessing costs of capture technologies that are at a very early stage of development is especially difficult, so qualitative assessments and assessments of potential energy efficiency improvements are often more appropriate.

- A wide range of technologies are being developed for post-combustion capture, including two-phase solvents, adsorption, membranes and cryogenic separation. Some of these technologies offer relatively modest cost reductions and others offer the prospect of more substantial reductions. Claims of the potential for cost reduction and energy consumption reduction found in the literature may be overoptimistic and some new technologies may struggle to compete with those that are already established.

- For plants with pre-combustion capture the cost of the CO_2 separation stage is substantially lower than for post-combustion capture. Technologies are being developed that offer the prospect of substantial cost reductions by reducing not only the cost of CO_2 separation but also the costs of other process units in pre-combustion capture plants such as shift conversion, CO_2 compression and power generation.

- The combination of pre-combustion capture with advanced solid oxide fuel cells has very high potential for cost reduction but faces significant development hurdles.

- The opportunities for significant cost reductions from the use of new technologies in coal-based oxy-combustion are limited, with the possible exception of alternative oxygen production technologies such as high temperature membranes.

- Gas-fired oxy-combustion processes which involve the use of new turbine cycles are at various stages of development. Some of these new cycles, particularly those that are at an early stage of development, may have the potential for substantial improvements in efficiency and costs compared to conventional post-combustion capture. However, oxy-combustion of gas is relatively inefficient as half of the oxygen required is converted to steam and does not directly contribute to the separation of CO_2.

- Various solid looping technologies that provide CO_2 capture are being developed. These technologies are at a relatively early stage of development and are subject to uncertainties but they have the potential to be one of the lowest cost technologies for capture at coal-fired power plants. Chemical looping combustion of coal has the best potential but application of this same technology to gas-fired power production does not compete with gas turbine based power generation.

- Industrial plants will in most cases employ capture technologies that are similar to those being developed for power plants, although the gas compositions and operating conditions will be different in some cases. Some new technologies that capture CO_2 which are specific to the steel industry are being developed.

Adding CO_2 capture to a power plant causes a substantial increase in the LCOE which for the current generation of coal based capture processes is of the order of 80 to 100%. The potential for lowering this increase in LCOE has been critically assessed to produce numerical estimates of how much this increase might be reduced. By choosing this metric the benchmark costs of the plants without capture are eliminated from the comparison which is focussed solely on the extra costs of electricity resulting from operation of the capture process. In earlier drafts estimates of the reduction in total LCOE were summarised on the basis of the information found in the literature and quoted in this report. However, in some cases the claims appear to be overoptimistic and in others rather conservative. Figure 69 below illustrates the potential of the leading technologies but excludes any figures for systems based on solid looping. For both CaL and CLC large potential reductions have been claimed and seem achievable, but these early projections do need to be backed up by more detailed engineering cost estimates.

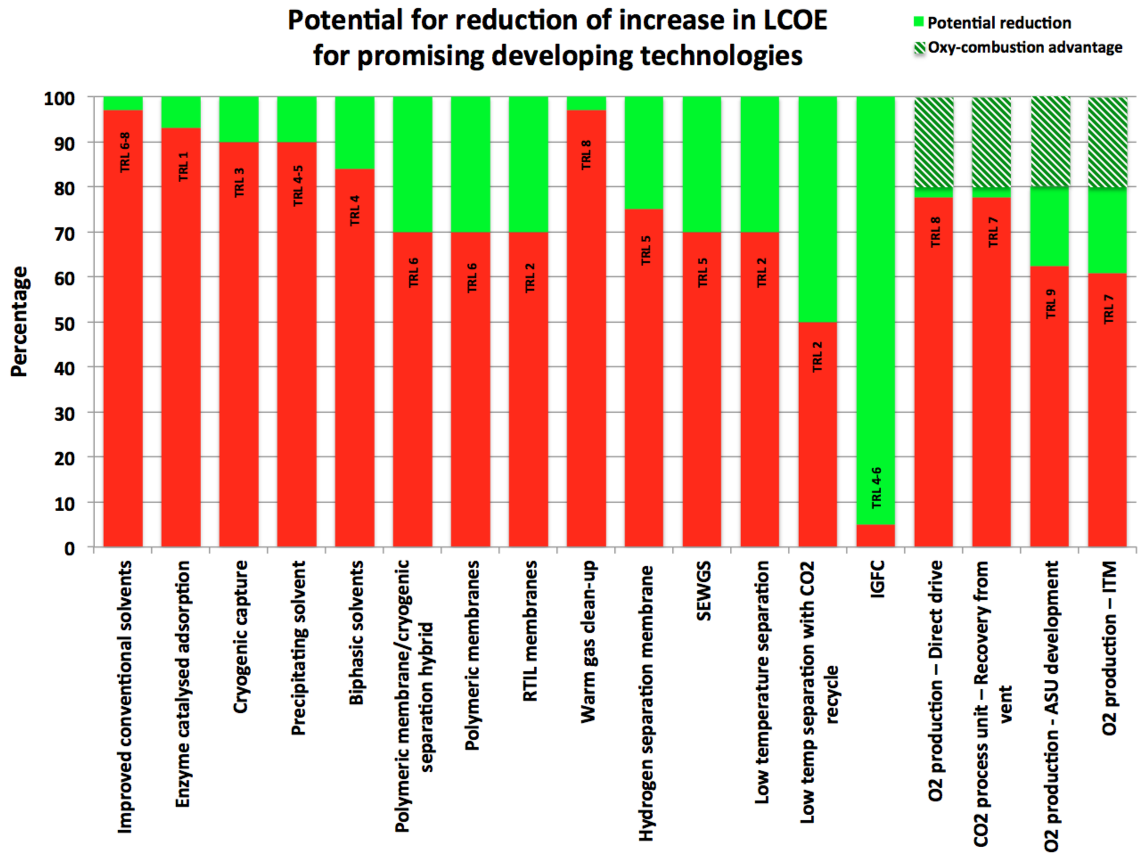


Figure 69 Potential of key technologies for LCOE reduction

The main indicator which has been used for assessing the potential of the various emerging technologies is the percentage increase in the LCOE. Nevertheless there is great interest in the cost per tonne of CO_2 abated as a measure because of the linkage to what is seen as the main financial driver, i.e. the cost of CO_2 emission certificates in the emerging emission trading systems. The cost per tonne is closely linked to the LCOE percentage increase but for a more complete calculation also the power plant efficiency change, fuel carbon content and a baseline electricity price need to be known. There is a strong relationship between the specific energy demand for capture and the cost per tonne abated as the specific energy determines the efficiency reduction.

Some costs of capture have been extracted from the literature and are mentioned in the report. However, in making an assessment of the potential for cost reductions, these have not been used as they did not always align with those based on considerations of the likely efficiencies, thermodynamics and equipment cost structures of the processes. It is also apparent that assumptions on inflation rates and discount rates vary between authors leading to cost estimates which cannot be directly compared.

9. List of abbreviations

Abbreviation	**Description**
2DS	UN climate scenario in which rise is limited to 2°C
4DS	UN climate scenario in which rise is limited to 4°C
a-CLR	Autothermal Chemical Looping Reforming
AMP	2-Amino-2-methyl-1-propanol
ARPA-E	Advanced Research Project Agency-Energy
ASU	Air Separation Unit
AZEP	Advanced Zero Emission Power (Process)
BF	Blast Furnace
BFG	Blast Furnace Gas
bioCCS	CCS applied to processes burning or using biomass
BOC	British Oxygen Company (now part of Linde)
BOF	Basic Oxygen Furnace
CA II	Carbonic Anhydrase 2
CaL	Calcium Carbonate Looping
CAP	Chilled Ammonia Process – (of Alstom)
CAPEX	Capital Expenditure
CARS	Ceramic Auto-thermal Recovery System
CCP	Carbon Dioxide Capture Project (Industry lead consortium)
CCS	Carbon Dioxide Capture and Storage
CDLC	Coal Direct Chemical Looping
CEPCI	Chemical Engineering Plant Cost Index
CES	Clean Energy Systems (US company)
CFB	Circulating Fluidised bed
CFD	Computational Fluid Dynamics
CHP	Combined Heat and Power
CIUDEN	Ciudad de la Energía (Spanish energy research organization)
CLC	Chemical Looping Combustion
CLEA	Cross-Linked Enzyme Aggregate
CLG	Chemical Looping Gasification
CLOU	Chemical Looping with Oxygen Uncoupling
CLP	Calcium Looping Process
CLR	Chemical Looping Reforming
CMS	Carbon Molecular Sieve
CO2CRC	Australian - Cooperative Research Centre for Greenhouse Gas Technologies
COG	Coke Oven Gas
COH	Cost of Hydrogen
COMELT	A DC electric arc based steel making process
CPU	CO_2 Processing Unit (in oxy-combustion process)
CSIC	Consejo Superior de Investigaciones Científicas (Spain)
CSIRO	Australian - Commonwealth Scientific and Industrial Research Organisation
CSTR	Continuous Stirred Tank Reactor
CU	Colorado University
CW	Cooling Water

DECAB	A process based on precipitating amino acid salts
DECC	UK Department of Energy and Climate Change
DMX-1	A 2-phase liquid capture process of IFP Energies Nouvelles
DOE	(US) Department of Energy
DR (DRI)	Direct Reduction (Direct Reduction of Iron)
EAF	Electric Arc Furnace
EBT	European Benchmarking Task
Econamine	A proprietary process using MEA based solvent licensed by Fluor
ECRA	European Cement Research Academy
EDA	Ethylene Diamine
EERC	Energy and Environmental Research Centre
EMAR	Electro-chemically Mediated Amine Regeneration
ENDEX	Coupled Endo/Exo thermic processes
EPRI	Electric Power Research Institute
ESA	Electric Swing Adsorption
EU	European Union
FCC	Fluidised Catalytic Cracking
FEED	Front End Engineering Design
FGC	Flue Gas Cooler
FGD	Flue Gas Desulphurisation
FTIR	Fourier Transform Infrared spectroscopy
GEA	IEA’s Global Energy Assessment
GT	Gas Turbine
HHV	Higher Heating Value
HISARNA	Advanced Steel process combining HIsmelt and Isarna
HIsmelt	An iron making technology of Rio Tinto
HPC	High Performance Caking
HRSG	Heat Recovery Steam Generator
HSE	Health Safety and Environment
ICES	Inertial CO_2 Extraction System
ICLC-CC	Integrated Chemical Looping and Combined Cycle
IEA	International Energy Agency
IEAGHG	International Energy Agency Greenhouse gas R&D programme
IFP	French Institute of Petroleum
iG-CLC	In-situ Chemical Looping gasification
IGCC	Integrated gasification and Combined Cycle
IGFC	Integrated Coal Gasification Fuel Cell
INCAR	Instituto Nacional del Carbón (Spain)
IPCC	International Panel on Climate Change
Isarna	An Iron smelting technology of Tata
ITM	Ion transport membrane
ITRI	Industrial Technology Research Institute (Taiwan)
KEMA	Keuring Van Electrotechnische Materialen (Dutch Institute)
KEPCO	Korea Electric Power Corporation
KS	Trademark for series of Mitsubishi’s hindered amine solvents
LANL	Los Alamos National Laboratory
LCL	Limestone Chemical Looping (Alstom)

LCOE	Levelised Cost of Electricity
LHV	Lower Heating Value
LMOG	Low Molecular Weight organic Gelators
LNG	Liquefied Natural Gas
LOX	Liquid Oxygen
LP	Low Pressure
LT	Low Temperature
LTFE	Low Temperature Frosting evaporator
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
MEMFO	The membrane research group at NTNU
MeO	Metal oxygen Carrier
MGD	Membrane Gas Desorption
MHI	Mitsubishi Heavy Industries
MPT (1)	Membrane Process Technology - Twente University
MPT (2)	Media and Process Technology Inc.
MTPY	Millions of Tonnes Per year
MTR	Membrane Technology Research
MW	Mega watts
NALCO	National Aluminium Co. India
NCCC	National Carbon Capture Centre
NEDO	New Energy and Industrial Technology Development Organization (Japan)
NETL	National Energy Technology Laboratory (of the USA)
NGCC	Natural Gas Combined Cycle
NJIT	New Jersey Institute of Technology
NOA	Norton Optical Adhesive
NREL	National Renewable Energy Laboratory
NTNU	Norwegian University of Science and Technology in Trondheim
OEM	Original Equipment Manufacturer
OFT	Oxy-Fuel Turbine
OPEX	Operating Expenditure
ORNL	Oak Ridge National Laboratory
OSU	Ohio State University
OTM	Oxygen transport membrane
PC	Pulverised Coal
PCC	Post-combustion Capture
PCM	Phase Change Material
PF	Pulverised Fuel
POSCO	Pohang Iron & Steel Co, Ltd (Korea)
POX	Partial Oxidation (process)
PSA	Pressure Swing Adsorption
PTSA	Pressure and Temperature Swing Adsorption
PV	Photo Voltaic
RIST	Research Institute of Industrial Science and Technology (Korea)
RTI	Research Triangle Institute
RTIL	Room Temperature Ionic Liquids
RWE	The energy company RWE AG

SER	Sorption Enhanced reforming
SINTEF	Norwegian Foundation for Scientific and Industrial Research
SMR	Steam Methane Reforming
SOFC	Solid Oxide Fuel Cell
SR-CLC	Steam Reforming with Chemical Looping Combustion
SWEGS	Sorption-Enhanced Water Gas Shift
TIT	Turbine Inlet Temperature
TNO	Toegepast Natuurwetenschappelijk Onderzoek – Dutch Applied Scientific Research Institute
TRL	Technology Readiness Level
TSA	Temperature swing Adsorption
UKERC	UK Energy Research Centre
ULCORED	A direct reduction steel making process
ULCOS	Ultra Low CO_2 Steelmaking (European steel research consortium)
UOP	UOP Honeywell (formerly Universal Oil Products)
VPSA	Vacuum Pressure Swing Adsorption
VSA	Vacuum Swing Adsorption
WGS	Water Gas Shift
WPI	Center for Inorganic Membrane Studies, Worcester Polytechnic Institute, USA
ZIF	Zeolite Imidazolate Framework

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