

Citation for published version:

MacDowell, N, Florin, N, Buchard, A, Hallett, J, Galindo, A, Jackson, G, Adjiman, CS, Williams, CK, Shah, N & Fennell, P 2010, 'An overview of CO₂ capture technologies', *Energy & Environmental Science*, vol. 3, no. 11, pp. 1645-1669. <https://doi.org/10.1039/C004106H>

DOI:

[10.1039/C004106H](https://doi.org/10.1039/C004106H)

Publication date:

2010

Document Version

Peer reviewed version

[Link to publication](https://doi.org/10.1039/C004106H)

University of Bath

Alternative formats

If you require this document in an alternative format, please contact:
openaccess@bath.ac.uk

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

An overview of CO₂ capture technologies

Niall Mac Dowell,^{a,b} Nick Florin,^a Antoine Buchard,^c Jason Hallett,^c Amparo Galindo,^b George Jackson,^b Claire S. Adjiman,^b Charlotte K. Williams,^c Nilay Shah,^b and Paul Fennell^{*a}

Received Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

First published on the web Xth XXXXXXXXXX 200X

DOI: 10.1039/b000000x

In this paper, three of the leading options for large scale CO₂ capture are reviewed from a technical perspective. We consider solvent-based chemisorption techniques, carbonate looping technology and the so-called oxy-fuel process. For each technology option, we give an overview of the technology, listing advantages and disadvantages. Subsequently, a discussion of the level of technological maturity is presented, and we conclude by identifying current gaps in knowledge and suggest areas with significant scope for future work. We then investigate the suitability of using ionic liquids as novel, environmentally benign solvents with which to capture CO₂. In addition, we consider alternatives to simply sequestering CO₂ – we present a discussion on the possibility of recycling captured CO₂ and exploiting it as a C₁ building block for the sustainable manufacture of polymers, fine chemicals and liquid fuels. Finally, we present a discussion of relevant systems engineering methodologies in carbon capture system design.

1 Introduction

Concerns of anthropogenically forced climate change owing to emissions of CO₂¹ are now well accepted and have resulted in a number of initiatives to reduce CO₂ emissions. Worldwide, there are more than 8,000 large stationary CO₂ sources whose cumulative emissions in 2005 were reported as being 13,466 MtCO₂/yr². Coupled to a growing population base with increasing demands for more energy intensive lifestyles, the scale of the problem is evident.

Owing to their energy density, proven resource base and established infrastructure for exploitation and distribution, it is well accepted that fossil fuels will continue to play an important role in both the generation of heat and power and in heavy industrial manufacturing operations for the foreseeable future³.

Carbon capture and storage (CCS) technologies are a promising route to achieving a meaningful reduction in CO₂ emissions in the near-term. Emission reduction targets such as 80–90% of CO₂ emissions from fixed-point sources are routinely discussed in the context of targets achievable by CCS technologies. It is accepted that the challenges associated with

the transport and storage of such large quantities of CO₂ are non-trivial, but are not insurmountable⁴. It therefore remains to select methods of CO₂ capture that are optimal not only in terms of their capital and operating cost, but also in terms of their environmental impact – there is little point expending vast amounts of resources to solve one problem, while at the same time creating another.

There are numerous technology options which are generally compatible with CCS activity, but of these, relatively few have gained any measure of acceptance from an industrial viewpoint. Three technology options that are generally accepted as being suitable for commercial deployment in the near to medium term are post-combustion CO₂ capture using amine solvents, oxy-fuel combustion and finally calcium looping technologies.

In amine-based CO₂ capture, the CO₂ rich gas stream is contacted with an aqueous amine solution. The amine solvent reacts reversibly with the CO₂, forming water-soluble salts. Given the reactive nature of the absorption, amine based solvent processes are well-suited to capturing CO₂ from dilute, low pressure streams. This makes this technology applicable to the majority of existing large, fixed-point sources of CO₂ and it is envisaged that it could be retrofitted with relative ease to the back end of an existing power station.

In oxy-fuel combustion processes, the fuel is combusted in a mixture of nearly pure O₂ (typically greater than 95% purity) and CO₂, recycled from the exhaust of the process. The main attraction of this technology is that it produces a flue gas which is predominantly CO₂ and H₂O. The H₂O content is easily removed by condensation, leaving a pure CO₂ stream which is suitable for compression, transport and storage.

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

^a Imperial College Centre for CCS, Dept. of Chemical Engineering, Imperial College London, South Kensington, London, UK, SW7 2AZ; Tel: +44 (0)20 7594 6637; E-mail: p.fennell@imperial.ac.uk

^b Centre for Process Systems Engineering, Dept. of Chemical Engineering, Imperial College London, South Kensington, London, UK, SW7 2AZ

^c Dept. of Chemistry, Imperial College London, South Kensington, London, UK, SW7 2AZ

In the solid looping technology which is considered in this paper, calcium oxide (CaO) and CO₂ are reversibly reacted to form calcium carbonate (CaCO₃). This process is somewhat analogous to conventional amine based absorption processes in that the CO₂ capture occurs in one vessel, known as the carbonator, then the “loaded” sorbent material, the CaCO₃, is then passed to a second vessel, known as the calciner, where the sorbent material is regenerated, producing a pure stream of CO₂. There are certain thermodynamic advantages to this technology, which lead to a lower than average efficiency penalty on a power station. The process also integrates very well with cement manufacture.

The ultimate fate of the captured CO₂ is also worth mentioning, at least briefly. In a later section of this paper, we suggest that there is a possibility of using at least a fraction of the captured CO₂ as a raw material which can be used to manufacture, among other valuable products, polymers and liquid fuels. However, it is likely that the majority of captured CO₂ will have to be sequestered, most likely in depleted oil and gas reservoirs, deep coal beds and deep saline aquifers⁴. However, alternative approaches such as the carbonation of minerals such as serpentine, Mg₃Si₂O₅(OH)₄, have also been proposed. In these methods for storing CO₂, 2 molecules of HO₂O are permanently displaced by 3 molecules of CO₂ - there are no concerns about leakage of CO₂, unlike the geological storage options. However, this storage option does not, at present, appear to be feasible for the large scale sequestration of CO₂ as the minerals must first be finely ground to approximately 5 mm and the carbonation reaction occurs in solution at high pressures - typically between 10 and 15 MPa⁵. Finally, in the implementation of this option, two kg of mineral are required per kg of CO₂ to be sequestered, and six times more stone than coal is required to be mined⁶. This obviously brings into question the viability of this process.

In the remainder of this paper, we compare these three technology options for post-combustion CO₂ capture and address the advantages and disadvantages of each option. We discuss in detail the complications associated with the design and selection of materials for use in these processes. The paper continues with some thoughts on future directions for this area in terms of process and material selection and design. We then present some perspectives on the feasibility of recycling captured CO₂ for use as an environmentally benign C₁ building block for chemical synthesis and also on the suitability of using ionic liquids for capturing CO₂. Finally, we conclude with a discussion of systems engineering methodologies and their relevance in carbon capture system design.

2 Capture Technologies

2.1 Chemical Absorption Technologies

2.1.1 Technology Overview

By chemical absorption technologies, we refer to gas-liquid contacting and separating equipment wherein gas and liquid streams flow in a counter-current fashion in a vertical column, where sufficient mixing and contacting are ensured by the inclusion of horizontal trays or packing material (random or structured), inside the column. In the typical operation of these processes, the “lean” solvent stream is introduced to the top of the absorption column, and flows vertically down the column over the packing material, absorbing its preferred component from the gas phase. The term “lean” refers to the fact that the solvent stream introduced at the top of the column contains little or none of the component that is to be absorbed. In the context of CO₂ capture, this means that the mole fraction of CO₂ in the liquid phase is small. The optimal value of lean loading of the inlet solvent stream (defined as the number of moles of CO₂ per mole of amine) is a complex optimisation problem which should be solved by a full process optimisation. However, it is generally considered to lie around 0.1 - 0.15 moles of CO₂ per mole of amine. Once the solvent stream reaches the bottom of the column, it is now termed “rich”, and it is directed to a solvent regeneration process, consisting of a further gas-liquid contacting column with a reboiler at the bottom and a condenser at the top. The purpose of the reboiler is to heat the incoming liquid stream to a suitable temperature in order to both break the chemical bonds formed in the absorption column and to provide a vapour stream to act as a stripping fluid. The purpose of the overhead condenser is both to provide a reflux liquid stream to the column and to ensure that the top-product stream is as pure as possible. It is this solvent regeneration process which comprises the bulk of the energy penalty associated with chemisorption-based CCS processes. For reference, a simplified flow diagram of this process is illustrated graphically in figure 1. The optimality criteria of such chemisorption processes are the minimisation of: (a) the amount of CO₂ emitted, (b) the equipment size and (c) fugitive emissions of volatile organic compounds (VOC). Finally, this must be done for the lowest possible operating cost, typically set mainly by the energy penalty associated with solvent regeneration.

In CCS applications, it is highly probable that a structured packing will be preferred as they are currently commercially available and are specifically designed to have both a large specific surface area (available surface area per unit volume) and a low pressure drop. Both of these facts conspire to reduce the amount of packing required and thus minimises the size of the equipment⁷.

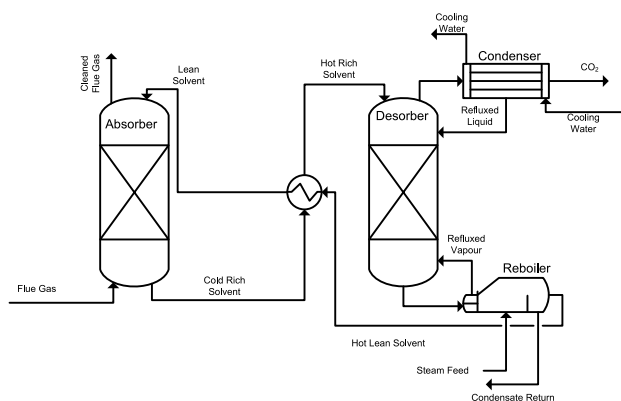


Fig. 1 Schematic of chemical absorption process for amine based CO₂ capture.

2.1.2 Pros and Cons

This technology option has the inherent advantage that it is an “end-of-pipe” technology, similar to those already in place for the mitigation of SO₂ emissions. Moreover, its addition to power plants, either as a retrofit or as new build, will not unduly affect the flexibility of operation demanded of these facilities⁸. However, as with all of the proposed capture technologies, chemisorption processes have the distinct disadvantage of their cost - both the capital expenditure (CAPEX) and operational expenditure (OPEX) associated with their deployment and operation is considerable. In the case of chemical absorption processes, it is anticipated that the deployment of this technology will result in a reduction of the thermal efficiency of a modern power plant from approximately 45% to approximately 35%⁹. This efficiency penalty accounts for the cost of solvent regeneration, CO₂ compression and transport as well as the ancillary costs associated with transporting flue gases and solvents. Moreover, owing to the low CO₂ partial pressure in the inlet flue gas, relatively high solvent flowrates are required to achieve a high rate of CO₂ capture. Some the amine based processes have been commercialised on a large scale, namely the Kerr-McGee/ABB Lummus Crest Process¹⁰, Fluor Daniel’s ECONAMINE process^{11,12} and the Mitsubishi KS-1 process licensed by Kansai Electric Power and Mitsubishi Heavy Industries¹³. However these processes are, according to the work of Bailey *et al.*¹⁴, expected to consume between 0.35 and 2.0 kg of solvent per tonne of CO₂ captured¹⁴. This obviously leads to significant costs associated with solvent make-up costs. Finally, given the relatively low degradation temperatures of most amines, the solvent regeneration processes takes place at approximately 120°C and 0.2 MPa, meaning that the CO₂ stream is produced at a low pressure, relative to that required for transport and storage, leading to considerable costs associated with the compression

of the CO₂ stream.

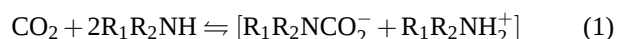
2.1.3 Technology Perspectives

Chemical absorption is a well-known technology, which has been widely deployed on an extremely large scale across several industries^{15–17}. It is therefore considered unlikely that any major innovation will occur in the design of either the process or the column internals, i.e., the packing, and any improvement here will be incremental at best⁷. Therefore, we contend that any major scope for reducing the costs associated with these processes lies in the selection and design of new, advanced sorbent materials as it is the solvent which determines the thermodynamic and kinetic limits of the process. It is also the solvent chemistry that determines the type and seriousness of any deleterious environmental and public health impacts associated with fugitive emissions of organic solvents, or their associated degradation or corrosion products^{18,19}. Therefore, the selection of appropriate solvents for use in these processes is a far from simple task.

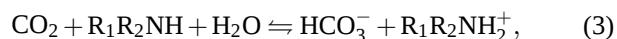
In terms of solvent selection, amines have traditionally been the solvents of choice, with a primary alkanolamine, monoethanolamine (MEA) typically considered to be the benchmark solvent with which alternative solvents must be compared¹⁵. Other compounds which are often considered are sterically hindered compounds such as 2-amino-2-methyl-1-propanol (AMP), secondary amines such as diethanolamine (DEA) and tertiary amines such as methyldiethanolamine (MDEA).

2.1.4 Amine Chemistry

The reactive nature of the aqueous solutions of amines with CO₂ system is well known, and there is a large body of experimental and theoretical work in place detailing the mechanism and rates of these reactions (see for example^{20–25} and references therein for details). In addition to the ionic speciation equilibria owing to the disassociation of CO₂ and the amines in aqueous solution, the principal reaction of interest between CO₂ and a primary and secondary amine (in aqueous media) is the formation of a carbamate, which is typically considered to occur via the formation of a zwitterion, and subsequent base catalysed deprotonation of the zwitterion. In combination these two reactions can be represented as^{23,24}

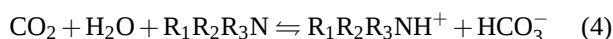


The other important reactions that contribute to the overall reaction rate are the reversion of carbamate to bicarbonate via a hydrolysis reaction (equation (2)), the formation of bicarbonate (equation (3)):



In the case of non-sterically hindered compounds, the reversion of carbamate to bicarbonate by reaction (2) is considered to be more important only at higher concentrations of CO₂ in the liquid phase. In the case of sterically hindered compounds, such as AMP, reaction (2) is particularly important as the presence of the methyl group significantly reduces the stability of the carbamate bond, resulting in the preferred formation of the bicarbonate, leading to the particularly high loading capacity (mole CO₂/mole amine) of this solvent²⁶.

The mechanisms involved in the absorption of CO₂ by aqueous solutions of tertiary amines, such as MDEA, are somewhat different to those of primary and secondary amines in that they do not react directly with CO₂, rather they act as a base, catalysing the hydration of CO₂²⁷. Thus the reaction of interest in aqueous solutions of tertiary amines is:



2.1.5 Degradation Chemistry

One aspect of the chemistry of these processes in which there is still a significant amount of uncertainty is that of degradation products. It is well known that amines are susceptible to degradation in the presence of O₂ and CO₂ as well as thermal degradation^{28–30}.

Oxidative degradation has been extensively investigated in the literature, particularly for MEA^{31,32}, DEA²⁸ and MDEA³³. Here, the main degradation products are volatile compounds, amines, aldehydes and also carboxylic acids.

Most, if not all, amines are irreversibly degraded by CO₂ and SO_x – both of which are likely to be present in the flue gases which are to be treated, and the concentration of these compounds and the temperature of operation are considered to be particularly important variables in the degree of degradation³⁴. It is known that secondary amines are more stable than primary amines, however the reaction paths are not well understood and there may be subtle effects of the amine structures on the stability of the degradation products¹⁵. For example, in an MEA system, the reaction with CO₂ generally results in the reversible formation of a carbamate, however, a small fraction may react further to form degradation products such as 2-oxazolidone which then reacts again with MEA to form N-(2-hydroxyethyl)-ethylenediamine (HEED) via intermediates of N,N'-di(hydroxyethyl)urea and 1-(2-hydroxyethyl)-2-imidazolidone^{15,35}. These reactions are quite well known, as reactions of MEA with CO₂ and O₂ have been well studied over the past decades, but with industrial flue gases, the process becomes much more complicated owing to the presence of a mixture of CO₂, O₂, CO, SO_x, NO_x and fly ash. Thus degradation processes under industrial conditions remain poorly understood³⁶.

Various studies have, however, shown that there is a similarity in the degradation mechanisms and products in primary,

secondary and tertiary amines^{29,30,37}. Typically, the main products are amines, oxazolidinones and imidazolidinones³⁸. Thermal degradation has also been studied in some detail, for at least some amines³⁰. It was found that the main thermal degradation products in the presence of O₂ were amines, amino-acid derivatives and carboxylic acids^{39,40}.

2.1.6 Environmental concerns

Relatively little is known about the expected emission profiles of the various solvents that may be used for CO₂ capture. In the case of MEA-based CO₂ capture processes, a recent IEA report indicated that for every tonne of CO₂ captured, 0.0032 tonnes of MEA will be emitted to atmosphere⁴¹. Given that a typical 2.4GW generator burning pulverised black coal produces approx. 30–50 tonnes CO₂/min⁴², the potential for solvent losses to atmosphere becomes obvious. The current lack of information concerning the details of the chemistry associated with the degradation products that are associated with the amine processes is a cause for some concern, as preliminary results indicate that many of the degradation products will be harmful to both human health and the environment^{42–44}. Aside from questions about the degradation chemistry, other important questions that have yet to be answered involve the atmospheric fate of emissions of amines and degradation products, i.e., are they deposited close to the emission source, what is the effect of atmospheric chemistry on these compounds, how can we determine emission legislation for these compounds and so forth. What is known is that most of the molecules considered for use in CO₂ capture applications are strongly polar, and are therefore highly water soluble. Thus, it is possible to envisage a scenario where fugitive amine emissions mix with rain water, and quickly become part of the water cycle and biosphere. Furthermore, it is known that some amine degradation products include amides and aldehydes as well as nitrosamines, which are potent carcinogens⁴³. It is conceivable that the packing material used in contacting equipment will play a role in this chemistry, e.g., carbon steel packing, has the potential to form metal salts^{44,45}. At this point it is possible to make the observation that of the thermophysical properties often considered in solvent selection for CO₂ capture, the volatility of the amines is very important, and should be given significant weight in any solvent design work in this area.

2.1.7 Solvent Blends

Amine-based processes for CO₂ capture are a very mature technology, with the first patent for the use of alkanolamines as absorbents for acidic gases being granted in 1930⁴⁶. Consequently, it is a very well understood class of technologies, and is considered to be economically feasible under certain

conditions¹. As mentioned previously, it is considered that the main scope for improvement to amine-based CO₂ capture lies in the design of improved solvent molecules and blends of existing solvents. In this context, blends of existing amines are considered to be the most realistic option, since, given the number of amine compounds currently available, the perceived likelihood of the discovery of a new molecule whose properties surpass those of existing compounds is slim. The reason that blends of amines are considered to be an attractive option in developing new sorbent materials is, for example, that it is possible to exploit the high absorption rates of primary and secondary amines as well as the high capacity of tertiary amines⁴⁷.

Sterically hindered compounds are considered to be especially interesting owing to their proclivity for forming weak carbamate salts, thus leading to both higher carrying capacities for CO₂ in terms of the number of moles of CO₂ absorbed per mole of amine and the fact that they also have a lower enthalpy of regeneration in terms of the amount of energy required per unit mass of CO₂ regenerated^{48,49}. However, it has been observed⁵⁰ that lower absorption enthalpies must lead to the generation of CO₂ at a lower pressure in the desorber and higher pumping and compression costs. Such considerations underline the importance of, as far as possible, simultaneously optimising the whole CO₂ capture process, rather than optimising parts on a piecewise basis. Typically, when sterically hindered compounds are considered, it is AMP which is investigated, and there has been considerable effort in developing predictive thermodynamic and process models describing the behaviour of AMP-based CO₂ capture processes^{51–55}. This preference for AMP over other hindered amines may be owing to it being a readily available monoamine, which makes its analysis easier since there is only one reactive amino group to consider and also that AMP is the hindered form of MEA as it is obtained by the substitution of two methyl groups for the two hydrogen atoms attached to the carbon atom in position α to the amino group in MEA. MEA is an extremely well studied compound, and detailed data for this compound are available. Consequently, a direct comparison with AMP is possible, with any differences in behaviour easily attributed to the effects of steric hinderance⁵⁶. Recently, however, other sterically hindered compounds such as 2-amino-2-methyl-1,3-propanediol (AMPD), 2-amino-2-ethyl-1,3-propanediol (AEPD) or tri(hydroxymethyl)aminomethane (THAM) have been studied, with blends of amines with THAM showing better performance in terms of volatility and energetics than AMP blends⁵⁷, indicating that THAM blends should be considered as potential alternative solvents with which to capture CO₂. Sterically hindered solvents have also been developed on an industrial scale, with MHI and Kansai electric having developed a proprietary hindered amine solvent known as KS-1^{13,58,59}. This solvent is reported as

being less susceptible to degradation and corrosion problems than a comparable MEA solvent, but it currently considerably more expensive than MEA⁶⁰.

Ammonia has also received significant attention as an alternative solvent, owing to the favorable loading (mole CO₂/mole NH₃) and energetics of an ammonia-based process^{61–64}. Ammonia can capture all the major acid gases (SO, NO_x, CO₂) which may exist in the flue gas of coal combustors. Since SO_x and NO_x emissions must comply with given limits, a single process to capture all acidic gases may reduce the total cost and complexity of any emission control systems^{61,62}. Moreover, ammonia is not expected to suffer from solvent-degradation problems (caused by SO₂ and O₂ as well as CO₂), is not expected to cause equipment-corrosion issues and could potentially reduce the energy requirements for CO₂ capture⁶⁴. The underlying chemistry behind the resistance of NH₃ to degradation is unclear - this point is typically asserted without any further explanation or clarification. One can speculate that this is because of the inherent simplicity of the NH₃ molecule, as alkanolamine sensitivity to O₂ is often attributed to the oxidation of the hydroxyl functional group to an acid⁶⁵, but additional clarification of this point is necessary. Large companies, such as Alstom^{66,67} are pursuing the commercialisation of NH₃ based CCS processes via the so-called “chilled ammonia process”, which is operated at temperatures between 273 – 283 K. This process results in the formation of ammonium bicarbonate, which has the benefit that the regeneration operations can take place at a pressure of approximately 3 MPa, resulting in significant savings in the energy penalty associated with CO₂ compression⁶⁰, as discussed briefly above. This process is undergoing pilot plant scale trials at We Energies’ Pleasant Prairie power plant as well as AEP’s Mountaineer Plant in New Haven⁶⁸.

Often, when blends of solvents are considered, mixtures of MEA with other alkanolamines are examined^{27,69–72}. The addition of AMP to an MEA solution almost invariably results in superior performance of the blend over that of MEA alone^{73–76}. One potential drawback is that, owing to concerns of solvent degradation and associated equipment corrosion, an upper limit of amine concentration of 30wt% is applied⁷⁶. Presumably, with the substitution of a degradation-prone compound, like MEA, with one less prone to degradation, such as NH₃, should allow higher amine concentrations. Some preliminary work on this particular blend⁷⁷ has shown that not only do a blends of AMP and NH₃ at least equal if not surpass MEA solutions in terms of absorption capacity⁷⁸ but also in terms of reaction rate⁷⁷.

Other additives to solvent blends that are sometimes considered are hydroxyl-containing compounds, such as alkanols. There is some evidence to suggest that the addition of short-chain alkanols to amine-water blends increases the solubility of CO₂ in the liquid phase⁷⁹. This is an interesting

step towards the development of solvents based on physical interactions for the capture of CO₂. Physical solvents, such as methanol, have been used for the removal of CO₂ from natural gas streams⁸⁰. This technology is not directly transferable to the problem of CO₂ capture from the flue gases of coal fired power plants, owing to the low CO₂ concentration and pressure of the gas stream. However, the inclusion of hydroxyl groups in a solvent blend might serve to increase the solubility of CO₂ in the liquid phase, while serving to reduce the energy required to regenerate the solvent. However, the addition of extra functional groups to solvents raises concerns regarding the tendency of the solvent to degrade.

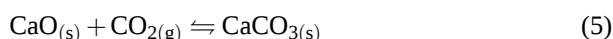
2.1.8 Gaps in knowledge and future perspectives

Post-combustion CO₂ capture is a very mature technology, with several pilot and demonstration plants currently in operation across the world. Several companies such as Alstom, Dow, PGE, E.ON, RWE npower, StatoilHydro, Total and others are actively engaged in this research and the deployment of this technology⁸¹. The principal barriers associated with the deployment of this option, apart from the obvious economic issues, are associated with the scale up of this technology. The inherent limitations of currently available absorption technologies when applied to post-combustion capture systems are well known and their impact on system cost can be estimated relatively accurately for a given application^{2,82–84}.

There are extensive development efforts associated with the development of novel solvents, such as the CESAR project⁸⁵ whose principle aims are towards a breakthrough in the development of low-cost post-combustion CO₂ capture technology. It is expected that the results of this project and others will result in post-combustion CO₂ capture technologies being the CO₂ emission mitigation technology of choice, at least during initial stages of the large-scale deployment CCS technology.

2.2 Carbonate looping technology

CO₂ capture using high-temperature solid sorbents has recently attracted a great deal research attention. A particularly promising solid sorbent candidate is calcium oxide (CaO), which can be derived from natural limestone. The process, commonly referred to as carbonate or calcium looping, exploits the reversible gas-solid reaction between calcium oxide (CaO) and CO₂ to form calcium carbonate (CaCO₃), according to equation (5).



The simplified process flow diagram, as applied to post-combustion capture, is shown in figure 2. In one vessel, the carbonator, the carbonation reaction between CO₂ and solid CaO separates CO₂ from a gas mixture, e.g., coal-combustion

flue gas, resulting in the capture of CO₂ via the formation of solid CaCO₃. The CaCO₃ is then transferred to a second reaction vessel, known as the calciner, where it is heated to reverse the reaction, releasing the CO₂, and regenerating the CaO-sorbent which is recycled back into the carbonation vessel. A circulating fluidised bed reactor, which is a mature technology at the large-scale, is considered most suitable for the carbonation and calcination vessels owing to very good gas-solid contacting and temperature uniformity across the reactor bed.

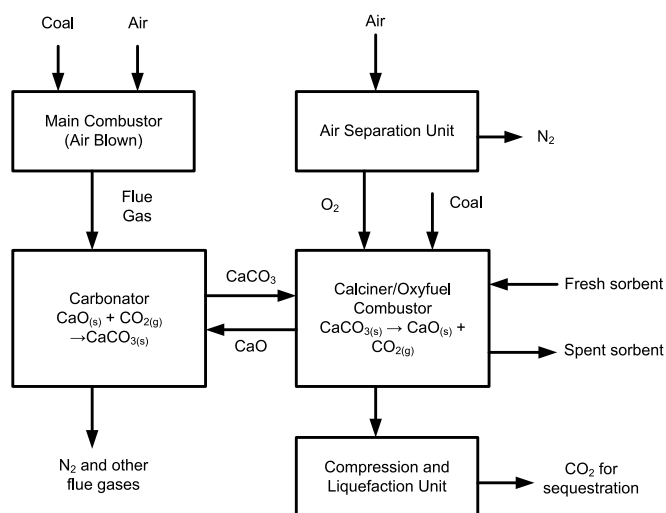


Fig. 2 Post-combustion carbonate looping reproduced from Blamey et al.⁸⁶

Carbonation is an exothermic reaction and is typically carried out at about 650 °C, owing to the inherent trade-off between the equilibrium driving force for CO₂ capture and the reaction kinetics. The carbonation reaction is characterised by a fast chemical-reaction-controlled reaction phase that abruptly transitions to a slow diffusion-controlled phase. The transition from rapid to slow phases is associated with the accumulation of a CaCO₃ product layer with coverage sufficient to significantly impede further conversion (the rate determining step in the reaction ceases to be the surface kinetics of the reaction and becomes instead the diffusion of CO₂ through the solid CaCO₃ product). As a result, the conversion of CaO to CaCO₃ is usually limited to about 70% in the first carbonation cycle for carbonation of around 10 minutes duration. Furthermore, the extent of conversion recedes throughout long-term carbonate looping, e.g. to <10% after 30 cycles⁸⁶. This diminished capacity to capture CO₂ is discussed in detail in §2.2.1.

By contrast, the endothermic calcination reaction proceeds rapidly to completion in a single step under a range of condi-

tions above about 750 °C. However, if the objective is to produce a pure stream of CO₂, then thermodynamic limitations dictate that under a high CO₂ partial pressure (<90 vol%) calcination must be conducted at 900–950 °C. To achieve this relatively high temperature, it is generally accepted that additional fuel must be combusted in the calcination vessel in pure O₂, requiring an air separation unit (figure 2)⁸⁷, though this is around a third the size of that which would be required for an oxyfuel-fired power station. Critically, the energy penalty associated with the air separation is partially offset by the recuperation of heat in the form of the hot CaO and CO₂ streams, and heat produced from the exothermic carbonation reaction, which can be used to generate additional steam, owing to the high temperature (650 °C) at which the heat is released. On this basis, the efficiency penalty associated with CO₂ capture from a power station using carbonate looping is extremely competitive; this is discussed in detail in §2.2.3.

In addition to the potential to minimise the energy requirements for CO₂ capture, other advantages of carbonate looping technology include: the unique prospects for synergies with heavy-emitting industry, e.g.: cement manufacturing (discussed in §2.2.3); use of mature large-scale CFBs, which reduces scale-up risk; and the relatively cheap sorbent derived from natural limestone. Furthermore, whilst carbonate looping has been introduced in the context of post-combustion capture, the technology also underpins a family of advanced energy systems under development for the production of electricity and/or hydrogen. These include: pre-combustion capture via coal and/or biomass gasification; selective production of hydrogen from hydrocarbons, commonly referred to as sorbent enhanced reforming (SER)⁸⁸; and energy storage⁸⁹. SER is also an essential feature of the Zero Emission Carbon (ZEC) concept, which represents a step-change in power generation efficiency predicted to be about 70%, including the isolation of a near pure stream of CO₂⁹⁰.

Post-combustion carbonate looping is the most developed application and has been identified by The Technology Task Force of the European Technology Platform for Zero-Emission Power Plants as one of the highest priorities for future R&D. H₂ production and energy storage represent more advanced applications, characterised by greater potential for the future, but also greater technical risks⁹¹. The discussion below relating to performance and cost-efficiency estimates is focussed on the post-combustion application of carbonate looping, which is rapidly being evolved from the pilot- to demonstration-scale.

At present, post-combustion carbonate looping is being tested in a 75 kW pilot plant at Canmet Energy (Ottawa, Canada)⁹², and pilot-test facilities at about the same scale are also located at the Instituto Nacional del Carbón (INCAR, Spain)⁹³, Cranfield University (UK)⁹⁴ and the University of Stuttgart (Germany)^{95,96}. However, the Spanish utility, En-

desa, and mining company, Hunosa, are constructing a 2 MW test facility for an EU funded project known as CaOling⁹⁷ and a 1 MW test facility, funded by the German government as well as industry funders, is under development at TU Darmstadt, Germany⁹⁸. In addition, a number of patents⁹⁹ are also held related to carbonate looping technologies, and Ohio State University is reportedly demonstrating these processes at industrial scale, although details about the projects are not readily available. Significantly, Cemex which is the world's third largest cement manufacturer have a pilot plant in Monterrey, Mexico¹⁰⁰. As previously discussed, there is a unique synergy between cement manufacture and carbonate looping because the exhausted sorbent (CaO) can be used instead of fresh limestone as a feedstock for cement manufacture, thus reducing the direct CO₂ emissions of the entire cement manufacturing process by about 50%. It is important to note that cement manufacture is responsible for 7% of global industrial CO₂ production, and that this sector is otherwise extremely expensive to decarbonise (McKinsey cost curve¹⁰¹).

2.2.1 Research Challenges

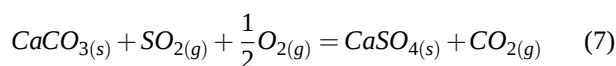
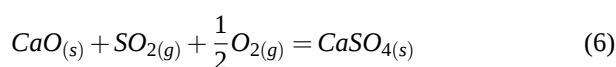
As previously mentioned, sorbent derived from natural limestone loses its capacity to capture CO₂ after multiple CO₂ capture-and-release cycles, and large amounts of fresh limestone are required to maintain an acceptable CO₂ capture efficiency. However, because of the low cost of the sorbent, this does not represent a critical flaw for post-combustion carbonate looping, and the economics are particularly favourable if the exhausted sorbent is used as a feedstock for cement manufacture. The main factors influencing this drop-off in capacity are: sintering, attrition, and chemical deactivation to the competing chemical reaction with sulphur dioxide (SO₂) – these are discussed in turn below.

Sintering refers to changes in the pore shape and size distribution, and grain growth, which tends towards a reduction in the total pore volume and reactive surface area. This process occurs during heating of particles, and the severity is increased at high temperatures, long exposure to high temperature, as well as by the presence of steam, CO₂ and impurities¹⁰². On this basis, CaO sorbent particles are most vulnerable to the effects of sintering during calcination; and owing to the different conditions used in long term cycling experiments (i.e., temperature, CO₂ and H₂O partial pressures), and the range of impurities in natural limestones, sintering behaviour should be evaluated on a case-by-case basis.

Carbonate looping involves handling a large quantity of solids in a highly abrasive environment which inevitably leads to attrition and the formation of fines susceptible to elutriation by the fluidising gas. Whilst there has been considerable work on attrition of CaO-based sorbents in the context of sulphur capture, there has been limited work relevant to carbon-

ate looping¹⁰³. In the case of CaO-based sorbents for sulphur capture, they are exposed to a single calcination phase known to make them more vulnerable to attrition; by contrast the sulphation reaction is reported to strengthen the sorbent¹⁰⁴. To some extent attrition is thought to increase SO₂ capture capacity by exposing fresh material which may be inaccessible to SO₂ owing to the formation of a non-porous product layer causing pure blockage and plugging^{105,106}. There is less known about the attrition of limestone particles in the context of continuous carbonate looping. It has been reported that limestone exhibits a high attrition rate during the first calcination, with a reduction in the rate of attrition during cycling based on bench- and small pilot-scale experiments^{107,108}. However, continued attrition during long-term looping may be a significant problem upon scale-up owing to the large volume of material and the quantity of fresh material used. In addition, the wide-ranging vulnerability of natural limestones to attrition suggests that they must be individually evaluated. A recent study has shown that particle size reduction owing to particle densification should also be considered when measuring the extent of attrition during long-term cycling, which is generally quantified based on changes in the particle size distribution¹⁰⁹.

Competing chemical reactions between CaO and fuel-bound impurities, most significantly sulphur, also affects the long-term CO₂ capture capacity of CaO-sorbents. In the case of coal, where sulphur may be present at concentrations up to about 8 wt%¹¹⁰, CaSO₄ may form by indirect (equation (6)) or direct sulphation (equation (7)) under the oxidising conditions in the carbonator and calciner (relevant to post-combustion carbonate looping). Whilst regeneration of CaSO₄ to CaO can be achieved, the temperature required is prohibitively high; and thus, sulphation represents an irreversible loss of sorbent which must be replenished. Despite this adverse effect of sulphur on CO₂ capture performance, it has been suggested that the reaction could improve the economics of carbonate looping by eliminating the need for a separate flue gas desulphurisation unit, particularly if the exhausted (sintered) CaO-based sorbent is used as a guard bed at the entrance to the carbonator.



2.2.2 Modified CaO-based sorbents

Strategies for improving the reactivity of CaO for long-term carbonate looping, include: (i) sorbent hydration^{111,112} (ii) doping with foreign ions¹¹³, (iii) thermal pretreatments¹¹⁴ (iv) the use of nanomaterials¹¹⁵; (v) the use of inert porous supports^{116–118} and (vi) pelletisation¹¹⁷. The essential aim of all

of these strategies is to limit the degradation of sorbent morphology associated with sintering and the cyclic carbonation-calcination reaction; and to obtain stronger sorbent particles resistant to attrition. Critically, all modified sorbents for carbonate looping are subject to a major economic constraint, because they must compete with cheap and abundant limestones. Furthermore, irreversible loss of reactive CaO caused by the presence of sulphur means some amount of fresh sorbent input may be unavoidable; hence the quality of the fuel used in the main combustor or calciner may prohibit the use of costly artificial materials.

The USDOE have recently presented a supported amine sorbent¹¹⁹. The production of this sorbent involves a large number of chemical and physical processes. It has a maximum theoretical capacity for CO₂ of 0.132 g CO₂ per g of sorbent, however this number reduces to 1.01 g CO₂ per g of sorbent under typical process conditions. A detailed discussion of this area is presented in the work of Blamey *et al.*⁶.

Overall, sorbent modification strategies have been successful in reducing the rate of decay from sintering and attrition; however, as far as we are aware, no sorbent modification has resulted in complete elimination of the problems. Whilst sorbent hydration has been demonstrated as a successful strategy to regenerate exhausted sorbent particles, mechanical stresses associated with the formation of Ca(OH)₂, which has a higher molar volume than CaCO₃, makes sorbent particles more susceptible to attrition⁸⁶. There is clear scope for the development of inexpensive sorbent modifications in order to improve the efficiency and minimise the cost of carbonate looping technology.

2.2.3 Performance and cost-efficiency estimates

As previously mentioned, the performance and cost-efficiency estimates discussed in this section relate to post-combustion carbonate looping, which is being rapidly evolved from the pilot- to demonstration-scale and is the most mature application of carbonate looping technology. Considerable reductions in the efficiency penalty are estimated for post-combustion carbonate looping. Previous researchers^{98,120} have calculated a 3% efficiency penalty drop (plus an additional 3% for CO₂ compression), which is consistent with the estimates published by Abanades *et al.*¹²¹ of 6–8% (including compression). These efficiency estimates are extremely competitive compared to the 10–12% drop in efficiency estimated for MEA-scrubbing¹²². It is important to note that these estimates include the decay in CO₂ capture capacity of the sorbents through multiple CO₂ capture-and-release cycles.

Improvements in overall efficiency equate to lower fuel requirements, less CO₂ produced, the minimisation of the adverse environmental impacts, and an associated reduction in the cost of electricity (COE). There is less cost-efficiency

data available in the literature for more advanced technologies such as post-combustion carbonate looping*, compared to MEA scrubbing or oxy-combustion, and greater uncertainty in the cost estimates may be expected. That said, three studies^{98,123,124} evaluate the cost-efficiency of post-combustion carbonate looping, reporting CO₂ avoidance costs to be of the same order of magnitude as oxy-combustion, and consistently lower than post-combustion capture with MEA. Abanades et al.¹²³ estimate an increase in the COE for post-combustion carbonate looping from 24–35%, including compression but not storage. The significant cost advantage of post-combustion carbonate looping compared to MEA scrubbing is because of the use of a cheap sorbent derived from natural limestone, e.g. priced at 0.0015 USD/mole compared to 0.544 USD/mole for MEA[†]. This is particularly significant considering the degradation of the sorbent/solvent due to the presence of impurities (e.g. sulphur) necessitating a significant input of fresh material. The sale of exhausted sorbent to the cement industry has also been proposed as method to improve the economics of carbonate looping technology^{121,125}, as well as reducing the CO₂ emissions associated with cement production by at least 50% associated with the calcination of limestone.

2.3 Oxyfuel combustion technology

Oxyfuel combustion is the combustion of the fuel in a mixture of CO₂ (recycled from the reactor exit) and pure O₂. A schematic diagram of an oxyfuel-fired system is shown in figure 3.

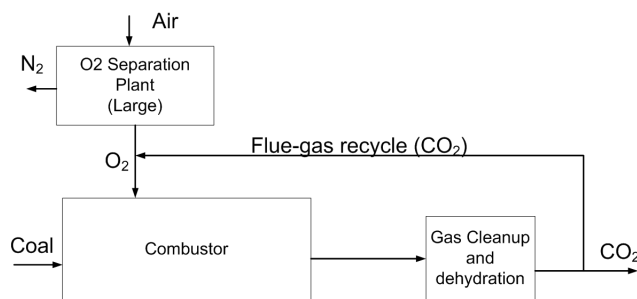


Fig. 3 Schematic of Oxyfuel combustion plant

Oxyfuel combustion imposes no parasitic losses on the steam cycle of the plant itself, since it is close to pure CO₂ which leaves the boiler. However, there is a significant energy penalty associated with the separation of air into its constituent parts, meaning that the efficiency penalty for an oxyfuel

power station will be similar to that of a power station fitted with amine scrubbing¹²⁶, unless some form of novel production method (discussed below) is used to produce the oxygen

2.3.1 Pollutant formation

NO_x

Owing to the lack of N₂ in the combustion atmosphere, less NO_x is formed during combustion (there is no possibility of thermal NO_x being formed)¹²⁷, and potentially lower conversion of fuel nitrogen to NO_x. Similar findings have been found during oxyfuel-fired combustion in a circulating fluidised bed¹²⁸. Test firing by Doosan Babcock^{129,130} conducted as part of the OxyCoal-UK phase 1 project, supported by the Department for Business, Enterprise and Regulatory Reform (BERR) indicated that overall NO_x emissions could be reduced by approximately 50% (on the basis of the heat input).

SO_x

Owing to the lower overall flowrate of the flue gas there is a higher concentration of SO₂ within it, but a lower overall flowrate of SO₂ produced. It is suspected that this is caused by the greater concentration of SO₂ driving the formation of secondary products¹³¹ including retention of SO₂ in the fly ash¹³⁰. Some have researched oxyfiring a fluidised bed. The situation is more complicated when the formation of SO₂ is considered in this case. Some research in a circulating fluidised bed¹²⁸ has found reduced SO₂ uptake when the bed is oxyfired, as compared to firing with air, though the results were variable depending upon the temperature, with better SO₂ uptake at higher temperatures during oxyfiring of petroleum coke which the authors suggested was caused by a change to direct sulphation as opposed to indirect sulphation. However, they were unable to replicate this change when coal was used as the fuel.

Hg

Mercury is a serious issue for any CCS system, owing to its potential effects on the compression systems, which currently have aluminium parts within them. Mercury causes pitting corrosion on aluminium¹³², which has caused serious issues for compression systems in the past¹³³. The potentially higher concentrations of SO₃ in oxyfiring may lead to competition for Cl between SO₃ and Hg and reduce the efficiency of the transformation of Hg into HgCl₂. This is important because HgCl₂ is more easily removed than elemental Hg from flue gas¹³⁴.

Ash / Fouling

Studies of ash deposition have yielded mixed results, most probably owing to the lack of suitable standard conditions for fouling experiments; since there have been no full-scale tests and no optimisation of a real power plant as yet, so different groups will have different flame conditions. Some work indicates that there is a relatively small effect of oxyfuel firing on

*This analysis assumed a circulating fluidised bed carbonater and an oxy-combustion calciner coupled with an air separation unit (ASU) about 1/3 the size of an oxycombustion power plant with an equivalent output.

†That is the amount of sorbent needed to capture 1 mole of CO₂ based on the price of raw materials in USD for year 2000

fouling¹³⁵, with a small increase in the amount of ash fouling on tubes. Others have found in a 1MW test facility¹³⁶ that the deposits from oxyfiring were similar in size and composition to those from air firing on the same rig, though perhaps more densely packed. However, in these tests, the temperature in the flame was lower in the oxyfired case than in the air fired case. Only full-scale testing will allow optimisation of the entire system, including the reduction of ash fouling, to take place.

Corrosion

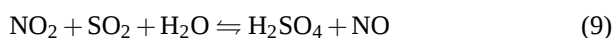
Test firing by Doosan Babcock¹³⁷ has found that the high CO₂ and potentially high SO₂ environment inherent for oxyfuel combustion can lead to enhanced corrosion in the temperature range of 550 - 800°C. The average measured rates of corrosion, relative to those measured at the same temperature for a normal flue gas were 1.6, 1.4 and 2.2 for a gas containing high SO₂ concentration, one with high CO₂ concentration and one with elevated concentrations of both. The impact was found to be higher for lower grade materials.

2.3.2 Pollutant Removal

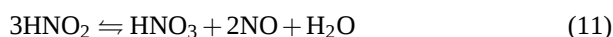
It is frequently assumed that gas treatment will be similar for both CCS-enabled and standard air-fired CO₂ capture. This may not be the case for oxyfuel firing, since the cleaning will take place on gas of a quite different composition. An interesting development, recently trialled by Doosan Babcock in collaboration with Imperial College¹³⁸ indicates that simultaneous removal of SO₂, NO and other gaseous pollutants (including Hg) is possible during compression of the CO₂, given sufficient residence time and the presence of liquid H₂O after the compression stage. The authors discuss that since the reaction of NO and O₂ to form NO₂ according to reaction (8)



is rapid at high pressure and low temperature, it forms during compression. The NO₂ then reacts with SO₂ and H₂O (the Lead Chamber process), reaction (9), to form H₂SO₄ and NO, which will be converted to NO₂ by reaction (8).



Finally, the reactions of NO₂ and H₂O will yield Nitric acid



Preliminary experiments indicated that within a relatively minor residence time (seconds to minutes) at high pressure (14 barg), 98% of the SO₂ and 90% of the NO (initial concentrations 900 and 520 ppm) could be removed.

2.3.3 Potential Problems and Solutions

One problem with oxyfuel technology which does not affect post-combustion scrubbing to the same degree (particularly for retrofit to an existing boiler) is the potential for ingress of ambient air to reduce the concentration of CO₂ at the outlet, owing to the sub-atmospheric pressure operation of most boilers. Two potential solutions are¹³⁹ to reduce the pressure differential between the ambient air and the boiler (though still to maintain a mildly sub-atmospheric pressure) and to seal critical points for air leakage with a mantle of CO₂.

The separation of air into N₂ and O₂ prior to the combustion process is the key extra cost for oxyfuel combustion. Four main technologies have been identified¹⁴⁰ for this separation step. These are:

1. Cryogenic air separation. The current industry standard. High potential to reduce costs and energy penalty and able to produce large quantities of O₂ (current separation trains for up to 5000 t/day are available)¹⁴¹.
2. Polymeric membranes and molecular sieves. These have been assessed as having a medium likelihood of reducing power consumption and cost, but are only suitable for small volumes.
3. Oxygen production by chemical air separation^{141,142}. Here, a mixture of the nitrate and nitrite salts of elements such as sodium or potassium are contacted with air, the O₂ from which reacts to convert NO₂⁻ to NO₃⁻, which is then transported to a desorber where the reaction is reversed. This process (Moltox) was investigated by Air Products (supported by funding from the US DoE); it was suggested that energy savings of 40% were possible in comparison with cryogenic production of O₂¹⁴¹. However, further development and demonstration of the technology is necessary prior to deployment.
4. High Temperature Ceramic Membranes. Tested by Air Products at pilot scale (5 t/day) since 2005 with DoE funding. Potential problems with the technology include the difficulty of achieving high quality seals at the ends of the membranes. However, high temperature ceramic membranes are one of the most promising technologies for O₂ separation, with the potential for deployment at both large scale and at low cost.

Overall, in the near future, it is likely that O₂ for oxyfuel combustion at scale will be produced almost exclusively by cryogenic air separation. It seems likely that high temperature ceramic membranes will be the next potential technology with widespread application.

2.3.4 Trials

The technology is arguably the simplest method for CCS, is retrofittable and has recently been trialled by Vattenfal at the scale of 30 MWt¹⁴³. Doosan Babcock have recently equipped their 40 MW test burner facility in Renfrew, UK, for oxyfuel firing^{144,145} (see figure 4).



Fig. 4 40 MW test burner facility at Doosan Babcock's Renfrew facility. Image copyright of Doosan Babcock Energy Limited

They have found that, when the volumetric flowrate through the burner and the oxygen content of the primary gas is maintained at the same level as for air firing, with an overall stoichiometry of 1.2, the flame structure and shape were similar for air firing and oxyfuel combustion (see figure 5). In addition, a similar furnace exit gas temperature (FEGT) and heat flux towards the exit is observed¹⁴⁵. The Callide A power plant in Australia is to be retrofitted with oxyfuel technology, with CO₂ transport via tanker¹⁴⁶. The initial retrofit will see the equivalent of 30 MWe converted to CO₂ capture.

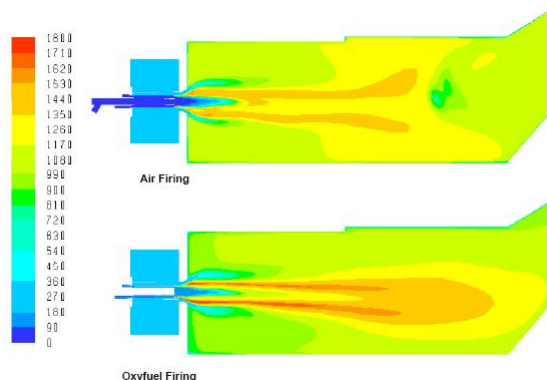


Fig. 5 Comparison of flame structure and shape for both air-fired and oxyfuel fired processes. Image copyright of Doosan Babcock Energy Limited

Air liquide have presented results for a novel burner with no mixing of oxygen external to the burner¹⁴⁷. They state that this has advantages for flame stability, turndown ratio and allows the use of difficult fuels. They furthermore claim that this system has improved operating safety, owing to the use of a dedicated oxygen circuit all the way along the distribution system.

2.3.5 Modelling

Current challenges lie in transferring the large body of knowledge in CFD simulation of combustion in air so that it describes oxyfuel combustion. Challenges include¹⁴⁸ the requirement to include radiative effects in the modelling; this is more important in oxyfuel combustion than in air, owing to the ability of CO₂ to absorb and emit infra-red radiation. The interaction of radiation with turbulence is also important. There is little validation of CFD in an oxyfuel environment, though this is now changing. Hitachi have conducted CFD modelling and plant design for retrofit of an existing modern power station to oxyfuel firing¹⁴⁹ and have concluded that it is feasible, if expensive in terms of extra fuel utilisation, with net electrical output reduced by more than 24%. Doosan Babcock and Scottish and Southern energy have conducted CFD simulation of their clean combustion test facility¹³⁷, with support from drop-tube furnace experiments conducted by the University of Nottingham. They found that there should be no major difficulties associated with oxyfuel firing. They predicted¹³⁷ a slightly narrower flame, with increased burnout (owing to higher partial pressure of O₂ and gasification reactions). Minor changes were predicted in the heat distribution within the furnace, with reduced heat absorption by the lower furnace walls and enhanced radiative transfer of heat to the superheater. Validation of the modelling against experimental measurements is ongoing. With regards to efficiency penalty, equilibrium flowsheeting modelling by Karakas et al.¹⁵⁰ indicates an even higher reduction in net electrical efficiency for a retrofit (from 41.5% to 28.8%) though with a smaller penalty for a new build system.

3 Future Directions

3.1 The use of ionic liquids for CO₂ capture

Ionic liquids (ILs) are commonly defined as liquids that are composed entirely of ions and that melt below 100°C. During the last decade ionic liquids have undergone a transformation from interesting, but poorly understood materials to the subjects of huge research activity. There has been an explosion of both academic research and industrial application. There are currently at least eight chemicals processing applications in use in the chemicals industry¹⁵¹.

Much of this interest is centred on the possible use of ionic liquids as “green” alternatives to volatile organic solvents. This claim rests on the fact that ionic liquids are non-volatile under ambient conditions. Hence, the exposure risk to ionic liquids is much lower than it is for a volatile solvent, so removing one of the most important, and costly to control, vectors for their absorption by the body. This is particularly important for workers in the chemical industry. The non-volatility also leads most to ionic liquids being non-flammable at ambient, and considerably higher, temperatures. However, there are many potential solvents in existence that meet these criteria but have not been the subject such intense interest.

Ionic liquids have been proposed as “designer solvents” because the ability to independently manipulate the cation and anion provides an easy means of customizing many solvent properties. Solvent polarity, acid/base character, density, viscosity and thermal stability can all be tuned to specific process needs. Ionic liquids have also been proposed as alternative media for CO₂ capture. Much of this interest stems from several interesting properties of ILs: a large liquid range, high thermal stability, extremely low volatility, good solubility of CO₂ and the ability to manipulate solvent properties through ion selection. The most commonly proposed use of ILs for CO₂ capture is in a pressure-swing configuration¹⁵² where CO₂ is preferentially absorbed from other gases. CO₂ could then be separately desorbed from the IL through a temperature increase or pressure decrease, with effectively zero solvent loss, owing to the nearly zero volatility of ionic liquids. If the CO₂ is physically absorbed into the IL this desorption process could be very efficient.

The thermal stability of ILs provides considerable potential for CO₂ capture applications - typical ionic liquids are stable to over 300°C¹⁵¹. Combined with the extremely low volatility, this provides an opportunity to regenerate the solvent at a very wide range of temperatures and pressures, providing an excellent opportunity for process optimisation that is not available using traditional aqueous liquid capture media. Specifically, the opportunity to regenerate at higher temperatures and pressures without fear of solvent degradation could provide a significant savings in the cost of CO₂ compression. ILs are also inert to oxidation, even at high temperature¹⁵¹. By reducing or eliminating process losses through thermal degradation, oxidative or chemical destruction and vapour loss the amount of solvent needed for the process may be greatly reduced. This will help to offset one of the largest drawbacks to large-scale use of ionic liquids - their relatively high cost when compared to traditional molecular solvents.

3.1.1 Comparison of ionic liquids to molecular solvents for CO₂ capture

The power of ILs compared to traditional molecular solvents comes from the “tunability” of the solvent properties. Cation and anion choices can be made independently to maximise favourable properties. For CO₂ capture, the most common manipulation is to include functionalised anions capable of reversible chemical reaction with CO₂¹⁵³. This will vastly increase the overall CO₂ solubility in the IL at the possible expense of easy desorption. However, as an added benefit, the selectivity of CO₂ compared to other gases can be significantly increased. This provides an opportunity for a high degree of control over the solubility of specific gases in a liquid medium.

Figure 6 shows some typical ionic liquid cations and anions. Typical cation classes that have been explored for CO₂ capture include (a) 1,3-dialkylimidazolium^{152,154}, (b) 2,4-28 N,N-dialkylpyrrolidinium¹⁵⁵, (c) N-alkylpyridinium^{156,157}, (d) tetraalkylammonium^{158–160} and (e) tetraalkylphosphonium^{155,158,159}. Some common anions would include (f) halide, (g) bis(trifluoromethyl)sulfonylimide (NTf₂), (h) triflate (OTf), (i) hexafluorophosphate (PF₆), (j) tetrafluoroborate (BF₄), (k) dicyanamide (dca) and (l) acetate (OAc). The wide range of available functionalities for cation and anion give rise to the enormous design flexibility offered by ionic liquids for a wide range of applications.

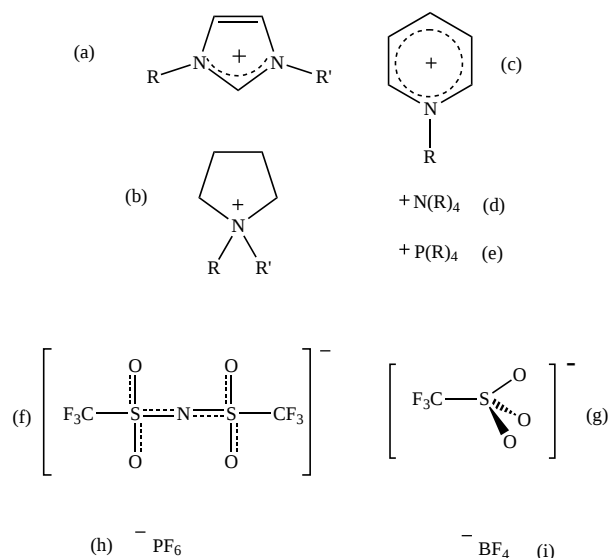


Fig. 6 Ionic liquid cations and anions

3.1.2 Anion Effects

The anion has been found to provide the most accessible means of altering the solubility of gases in ionic liquids,

mainly through specific interactions with the solute gas. Ionic liquids based on the dialkylimidazolium cation have been the most explored, owing to their low melting points, high thermal stability, relatively low viscosity and commercial availability¹⁵¹. While functionalisation of the alkyl side chains is quite common¹⁵³ the standard anions would be either 1-ethyl-3-ethylimidazolium [C₁C₂im]⁺ or 1-butyl-3-ethylimidazolium [C₁C₄im]⁺. These ionic liquids have been the most thoroughly examined for most applications, including CO₂ capture¹⁵¹. The solubilities of various gases (including CO₂ and N₂) at a variety of temperatures and pressures have been determined^{152,154}. A sampling of Henry's constants for CO₂ and N₂ in some [C₁C₄]-based ionic liquids is available in table 1. The highest solubility of CO₂ was found to be for the [NTf₂][−] anion, which is one of the least basic anions that has been explored. The general trend of decreased gas solubility with increased anion basicity indicates that physical absorption (controlled by the relative strength of the Coulombic forces in the ionic liquid leaving "room" for gases to dissolve) is dominating chemical absorption (the acidic nature of CO₂ would tend to increase solubility in liquids made up of more basic anions). The dominance of bulk physical effects over bulk chemical effects provides an opening for strongly basic anions that do not strongly associate with their cations to perhaps improve CO₂ solubility, or at the very least increase CO₂/N₂ selectivity. Additionally, these physical effects are likely to be more strongly temperature dependent than more specific chemical interactions, which would tend to ease CO₂ desorption.

Table 1 Henry's constants for CO₂ and N₂ in [C₁C₄] based ionic liquids

Cation	Anion	H (bar)	T (K)	Reference
[C ₁ C ₂ im]	[NTf ₂]	49.1	303	^{158,161}
[C ₁ C ₂ im]	[Bf ₄]	80.0	298	¹⁶²
[C ₁ C ₄ im]	[Bf ₄]	59.0	298	¹⁵⁵
[C ₁ C ₄ im]	[Pf ₆]	53.4	298	¹⁵⁵
[C ₁ C ₄ im]	[NTf ₂]	33.0	298	¹⁵⁵
[C ₁ C ₆ im]	[NTf ₂]	31.6	298	¹⁵⁶
[C ₁ C ₆ pyr]	[NTf ₂]	32.8	298	¹⁵⁶
[C ₁ C ₄ py]	[NTf ₂]	38.6	298	¹⁵⁵
[C ₁ C ₁ C ₁ C ₄ N]	[NTf ₂]	61.0	303	¹⁵⁹
[C ₆ C ₆ C ₆ C ₁₄ P]	[NTf ₂]	37.0	303	¹⁶³

3.1.3 Cation Effects

Despite the wide variety of reported cation structures for CO₂ capture, some generic cation effects can be determined. The most important aspect of these cation effects is that they are relatively minor when compared to the anion effects, at least for the cations studied to date. However, the effects are not in-

consequential. For example, the Henry's Law constants indicate that the CO₂ solubility in N-butyl-N-methylpyrrolidinium NTf₂ is within 20% of that measured in [C₁C₄im][NTf₂]¹⁵⁶. [C₁C₁C₁C₄N][NTf₂] fared even worse, with Henry's Constants nearly 35% higher than for [C₁C₄im][NTf₂], indicating even poorer CO₂ solubility. The variation in CO₂ solubility with changing cation is possibly caused by the minimisation of unfavourable interactions between CO₂ and the positive charge centre, which is much more delocalized when an imidazolium ring is employed¹⁶⁴. These differences are also much more significant than that observed between two cations with delocalised charge. The CO₂ solubility in 1-hexyl-3-methylpyridinium [NTf₂] was found to be just 4% lower than for the analogous [C₁C₆im][NTf₂]^{158,159}. CO₂:N₂ selectivities follow similar trends, with imidazolium-based ionic liquids outperforming the other cation types, though the effect is generally less pronounced than for solubilities.

Comparing ammonium-based cations to phosphonium-based cations is somewhat problematic owing to the typical disparity in the length of the alkyl side chains. However, CO₂ solubility and selectivity in [C₆C₆C₆C₁₄P][NTf₂] were found to be significantly lower than for either quaternary ammonium or imidazolium based ionic liquids^{158,159}. The charge distribution on quaternary phosphonium centres is quite complicated, and this effect may be responsible for the lower CO₂ solubility (and selectivity). Coupled with the problematic synthesis of these salts and generally inferior physical properties (such as drastically higher viscosities)¹⁶³, the phosphonium-based ILs would seem a poor choice for CO₂ capture applications.

The other major source of cation modification is via adjustments to the alkyl side groups on an imidazolium ring. This can be done either to introduce CO₂-philic moieties (such as fluorocarbon chains^{165,166}) or to improve the selectivity by excluding unwanted species such as water. This last aspect represents an important process consideration when choosing an ionic liquid - many of these liquids are hygroscopic (particularly the halide-based ionic liquids) while some are actually hydrophobic (such as PF₆ or NTf₂-based ionic liquids)¹⁵¹. Since water can have a detrimental impact on the separations efficiency of ionic liquids¹⁶⁷ the exclusion of excess water is an important design goal. Besides anion choice, the hydrophobicity of an ionic liquid can generally be altered via an increase in the chain length or hydrophobicity of the alkyl chain¹⁵². This can mean the introduction of a functional group, R, that is n-alkyl, branched alkyl^{168,169}, vinyl¹⁷⁰, allyl¹⁷¹, alkynyl^{172,173}, fluoroalkyl^{165,166,174}, benzyl^{175,176}, hydroxyl^{177,178}, ether^{178–180}, amine^{153,181,182}, nitrile^{170,172,183}, silyl^{168,169,184} or siloxyl¹⁸⁴.

As a general rule, the introduction of hydrophobic groups will make ionic liquids more hydrophobic (easing the exclusion of water) and improve absolute CO₂ solubility slightly

while the inclusion of more polar functionalities will improve IL-CO₂ interactions and therefore increase the CO₂/N₂ selectivity by as much as 75%¹⁵². This trade-off is at the very heart of ionic liquid selection criteria.

3.1.4 Comparison of ionic liquids

Great care must be taken when comparing ionic liquids - even to each other but especially to molecular solvents - in terms of molar solubilities of gases (mole fraction of dissolved gas)¹⁵². The vast molar volumes of ionic liquids (a consequence of high molecular weight) can make these values seem much larger than the volumetric solubility (capacity). It is often easiest to utilize mole fraction data (or Henrys constants) to gain molecular insight into CO₂-ionic liquid interactions¹⁵¹, but the volumetric solubility is a much more important engineering parameter. Such a comparison was made by Bara¹⁵² where it was noted that the volumetric solubility of CO₂ in ionic liquids at ambient temperature is at the low end of the range observed in common organic solvents. For example, the authors note that the ambient CO₂ solubility in ionic liquids is comparable to DMSO, while the Henrys constants are more similar to those for acetonitrile. This leaves ionic liquids occupying a middle ground in terms of CO₂ solubilities - higher than most polymers but lower than most organic solvents. The optimum ionic liquid class for CO₂ capture was proposed to be [C₁C_nim][NTf₂] owing to a confluence of superior physical properties and CO₂ solubility and selectivity¹⁵².

3.1.5 Mixtures of ionic liquids with amines

In order to overcome some of the limitations of ionic liquids as CO₂ capture media, while still taking advantage of their exciting physical properties, alkanolamines, such as MEA, have been employed as co-capture agents¹⁷⁷. These IL/amine mixtures combine the CO₂ selectivity and stoichiometric capacity (1:2 molar ratio of CO₂: amine) with improved stability on decomplexation imparted by the ionic liquid. This hybrid capture media possesses considerable potential to offer a best of both worlds approach.

Another hybrid solution involves the incorporation of amine functionality onto the ionic liquid cation^{153,177,184}. While this solution did substantially improve CO₂ capacity through the introduction of CO₂-reactive groups (up to CO₂:IL molar ratios of 1:2), these media can only charitably be referred to as liquids owing to enormous viscosities similar to liquid polymer solutions¹⁸⁵. This increase in viscosity will increase sorbent circulation costs and damage the potential for industrial implementation of these fluids. Some of this cost may be offset through other processing considerations - for example, the complexation energy between the IL and CO₂ will be similar to that for an amine and CO₂. However, by replacing water

with an IL (which will not boil) the only energy input necessary for regeneration is that required to break the CO₂-amine bonds; the waste energy previously used to boil the water off has been eliminated. This should reduce energy consumption associated with sorbent regeneration, though it is unclear whether this will be enough to overcome the other physical limitations associated with these hybrid ions.

3.1.6 Outlook on the future use of ionic liquids

Ionic liquids provide an exciting new option for carbon capture. While currently available ionic liquids display CO₂ solubilities that are approximately the same as molecular organic solvents, the potential for improving these values through modification of the ions making up the solvent promises exciting opportunities for future improvements. Combined with the high thermal stability and extremely low volatility of these solvents, the potential exists for the design of task specific ionic liquids that can compete with other CO₂ capture technologies in terms of performance while offering unique physical properties that will limit solvent losses and greatly increase the lifetime of the resulting capture media. The major drawback of ionic liquids, cost, should reduce a great deal as economies of scale come into play.

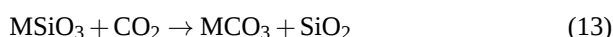
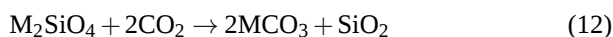
3.2 Recycling of captured CO₂

Carbon dioxide has long been identified as a renewable C₁ feedstock (being of low toxicity, highly abundant and economical) to access fine and commodity chemicals^{186,187}. Furthermore, ever increasing emissions of CO₂ highlights the urgent need to develop improved means to trap it and transform it to valuable chemicals. However, to date, only a handful of industrial processes actually use carbon dioxide. A number of these rely on the physicochemical properties of carbon dioxide, such as the use of supercritical CO₂ as a solvent (in particular for extraction processes such as decaffeination or recovery of essential oils)¹⁸⁸ or the use of gaseous CO₂ in the food industry (e.g. for use in drinks, or as a refrigerant)¹⁸⁹. CO₂ is also used in enhanced oil recovery (in its supercritical state, it can be used as a solvent) and in agriculture (as a photosynthesis enhancer), but none of these applications, excepting EOR, result in any net CO₂ consumption. The potential advantages of using CO₂ as a chemical feedstock are:

1. CO₂ is relatively cheap, highly abundant and could be used to replace toxic chemicals, such as phosgene or depleting resources such as petrochemicals
2. CO₂ can be transformed into totally new materials, such as new polymers, which could not easily be produced from conventional petrochemicals

- CO₂ can be transformed using efficient and economical routes (i.e. catalytic processes)
- Although the impact on global CO₂ concentrations of its transformation into products (e.g. chemicals, polymers, fuels) may be modest, the products are expected to significantly improve the economics of carbon capture and storage

As the most oxidized state of carbon, CO₂ lies at the bottom of a potential well and is the lowest energy state of all carbon-containing binary neutral species. Together with water, carbon dioxide is, in fact, the ultimate product of most energy releasing processes, including combustion and metabolic pathways. However, owing to the electron deficiency of the carbonyl carbon, the central carbon of CO₂ has a strong affinity towards nucleophiles and electron-donating reagents. CO₂ can thus be seen as an anhydrous carbonic acid, which rapidly reacts with basic compounds, because the bonding of a third atom to C (O or any other) is an exothermic process. Therefore, carbonates are lower in energy than CO₂, and, for example, the natural weathering of silicates is an exothermic process, but is very slow for kinetic reasons (equation (12) and (13), where M=Mg, Ca)¹⁸⁹.



The reactions above, and those in which CO₂ reacts with hydroxyl ion (yielding carbonate species) or amines (first step of the urea process) are good examples of processes in which CO₂ is converted without any external energetic input. On the other hand, the reactions that generate reduced forms of CO₂ require energy. Table 2 shows the free energy of formation of C₁ molecules¹⁹⁰: the biggest obstacle for establishing industrial processes based on CO₂ as a raw material is the large energy input which is required to reduce it in order to use it.

Table 2 Free energies of formation C molecules

Species	C Formal Oxidation State	ΔG_f (kJ.mol ⁻¹)
CH _{4(g)}	-4	-50.75
CH ₃ OH _(l)	-2	-166.1
C	0	0
HCOOH _(l)	+2	-345.09
CO _(g)	+2	-137.15
CO _{2(g)}	+4	-394.01

Two strategies enable its chemical transformation: the use of physical energy or the use of reactive chemical species (figure 7).

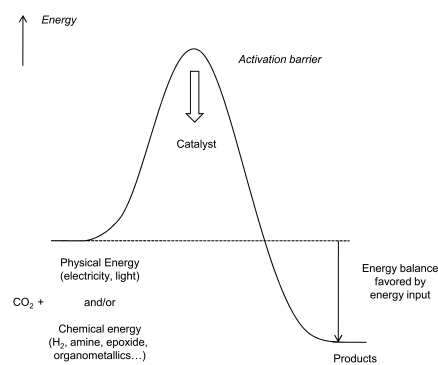


Fig. 7 Strategies for overcoming the energy requirement for the chemical conversion of CO₂

The use of physical energy is one option to favour the overall thermodynamic balance. The electrochemical and photo-electrochemical reduction of CO₂ to formic acid, formaldehyde, methanol and methane have thus been the focus of extensive efforts since the early 70s^{191,192}. Another strategy depends on reacting CO₂ with any reactive organic or organometallic compounds to produce new chemicals^{193–195}. From an industrial point of view, a catalyst is often required to lower the activation energy for the processes and therefore reduce the overall energy required for the transformation to occur. Any excessive heating must be avoided as it results in the production of carbon dioxide, by fossil fuel combustion, and thus negatively impacts the net consumption of CO₂.

In 2003, 110 megatons (Mt) of CO₂ were used for chemical synthesis¹⁹⁶. The products include urea (1) (146 Mt/y in 2008)¹⁹⁷, inorganic carbonates (2) (mainly 45 Mt/y of sodium carbonate in 2008 through the Solvay process)¹⁹⁸, methanol (3) (6 Mt/y), salicylic acid (4) (60 kt/y in 2003 through the Kolbe-Schmitt process)¹⁹⁹, cyclic carbonates (5) and polycarbonates (6) (a few kt/y)¹⁹⁴ (figure 8). For such processes, the carbon dioxide is always pressurized or in the solid state and derives from external sources (e.g. natural wells or as a by-product of the production of sodium phosphate, lime, hydrogen or as an off-gas from fermentations).

In addition to these commercial processes already using CO₂ as a feedstock, there are a number of other reactions that hold promise. The synthetic targets of those reactions can be divided into three categories: (i) fine chemicals, such as urea, carboxylic acids, and carbonates; (ii) fuels or commodity chemicals such as methanol, methane and formic acid; and (iii) plastics such as polycarbonates and polyurethanes. The scope for this part of the review is not to provide a comprehensive list of all known chemical transformations of carbon dioxide, but rather to highlight routes which have the potential to use the recovered carbon dioxide to produce chemicals with

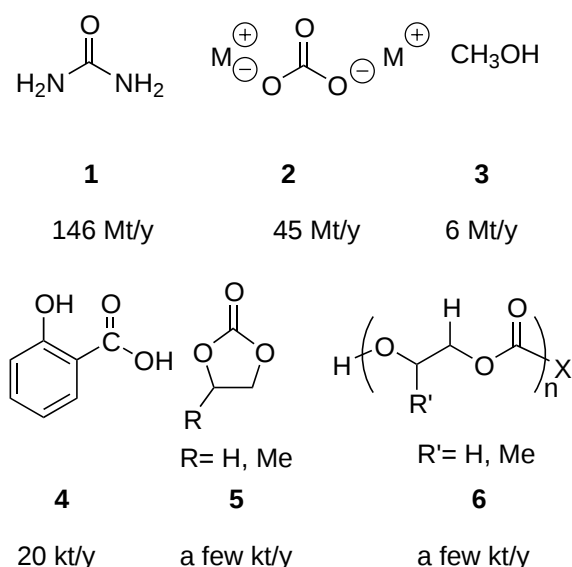


Fig. 8 Chemicals currently industrially synthesized from CO₂ and associated annual production using these processes

good market potential.

3.2.1 Fine Chemicals

CO₂ is so thermodynamically and kinetically stable that it is sometimes considered as inert. However, as mentioned before, the central carbon is electrophilic and can be easily attacked by nucleophiles. One of the best examples of this reactivity is that organometallic reagents such as Grignard reagents readily react with CO₂ even under mild conditions to produce carboxylic acids. Water, alcohols and amines can also react with CO₂ in a similar manner to produce compounds with a carboxyl or carboxylate group; further reactions of these species with electrophiles leading to the formation of carbonates and carbamates.

The reaction scheme shown in figure 9 outlines some of the synthetic targets incorporating CO₂; the products have been selected because of their market potential in terms of either the abundance of the co-reagent and/or the volumes of the product currently produced. Several excellent recent reviews provide considerably more details on more exotic and novel reactions of CO₂.^{186,192,194}

Among the industrial processes transforming CO₂ to fine chemicals, the most important are the conversion to urea (the Bosch-Meiser urea process, developed in 1922) and the synthesis of organic carbonates. Interestingly the synthesis of urea does not require any catalyst: it is purely a thermal reaction, and the reaction scheme is illustrated in figure 10. The synthesis consists of the exothermic reaction of liquid ammonia with dry ice to form ammonium carbamate, followed by

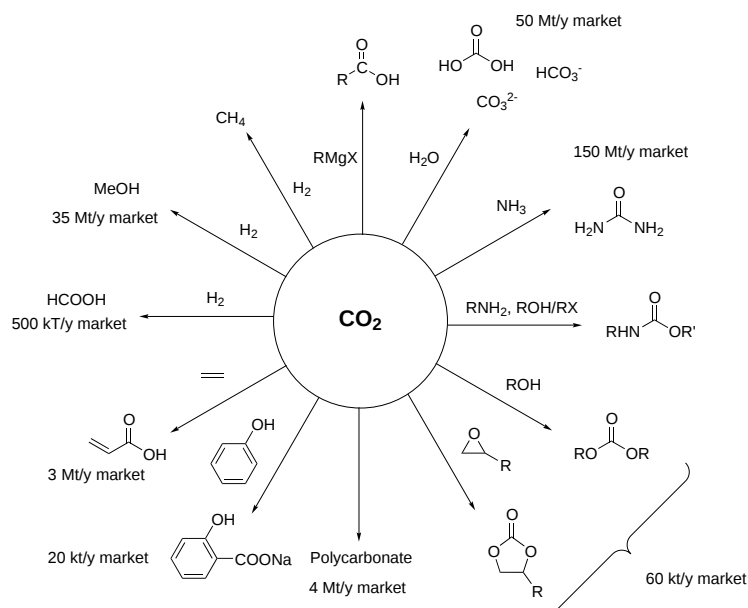


Fig. 9 Chemical transformation of CO₂ into commodity chemicals and market volumes

its endothermic decomposition into urea and water. Overall, the process is exothermic²⁰⁰.

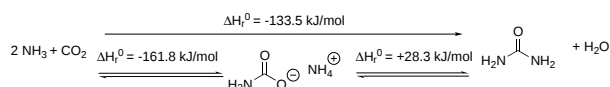


Fig. 10 Industrial synthesis of urea from CO₂ and thermodynamics of the process

In 2008, urea cost approximately \$250/t and its production was estimated at 146 Mt and is forecast to rise to 210 Mt/y by 2013; much of this rise being caused by increased demand for fertilizers. The major use of urea (>80%) is the production of nitrogen-release fertilizers, where it is particularly valued for its high nitrogen content and correspondingly low transportation costs per unit nitrogen. It is also a major building block for synthetic chemistry, with applications in the production of urea-formaldehyde and urea-melamine-formaldehyde resins and adhesives (e.g. for use in furniture, laminates, coatings, foams, wood glues), potassium cyanate (used as a precursor to carbamates, semicarbazides, isocyanates and for metal curing) and urea nitrate (an explosive).

Alkylen carbonate are also important products, with estimated volumes of approximately 60 kt/y²⁰¹. Ethylene carbonate (EC), propylene carbonate (PC), and dimethylcarbonate (DMC) are employed as electrolytes in lithium ion batteries, as aprotic polar solvents and as precursors for the manufacture of polycarbonates. Recently, the use of DMC as

a fuel additive has attracted much attention and could result of a extra potential market of 30 Mt annually^{202,203}. Using CO₂ to produce organic carbonates is a safe alternative to the traditional industrial use of phosgene or to the oxidative carbonylation of alcohols using CO²⁰⁴. The major drawbacks of phosgene processes are the high toxicity of phosgene (considered as a chemical weapon by international treaties) and the disposal of the hydrogen chloride produced. Using CO₂, on the other hand, has a minimal environmental impact as the byproduct is only water - the reaction scheme for this process is shown in figure 11.

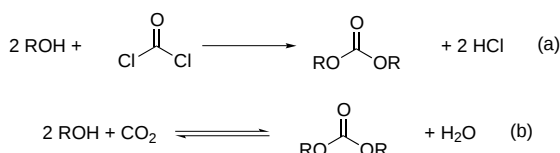


Fig. 11 Phosgene processes (a) vs CO₂ routes (b) towards the synthesis of organic carbonates

However, the equilibrium of the reaction from alcohols is unfavourable. In order to avoid this thermodynamic limitation, it is necessary to remove water from the reaction media using an adequate drying agent or to increase the CO₂ concentration by pressurizing it. A more favoured route has thus been proposed through the synthesis of cyclic carbonate. Linear carbonates and ethylene glycol can then be produced by alcohol addition (figure 12).

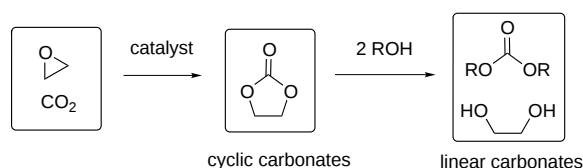


Fig. 12 CO₂/epoxide route towards cyclic and linear carbonates

Many catalysts (heterogeneous, homogeneous) have been developed for the cyclisation of carbene dioxide and epoxides²⁰². It is also worth noting that the process is closely related to the copolymerisation of CO₂ and epoxides, yielding polycarbonates. The majority of CO₂ transformations rely on the use of a transition metal catalyst that is able to activate CO₂.

Carbon dioxide is a linear 16 electron molecule (with a C-O distance of 1.163 Å, shorter than a ketone) but upon metal coordination of CO₂ (η-1 C, η-1 O, η-2...), the C-O bond is weakened and if the lowest unoccupied molecular orbital (LUMO) is partially occupied, a bent form of OCO is favoured²⁰⁵. The CO₂ is then activated and able to undergo a range of further transformations, such as the direct carboxylation of CX bonds^{206,207}, or carbon-carbon multiple bonds²⁰⁸.

In particular, the synthesis of acrylic acid from ethylene (107 Mt/y produced in 2005)²⁰⁹ and CO₂ is an attractive route compared to the oxidation of propylene (35 Mt/y produced in 2008)²¹⁰ and although the chemistry is still in the early stages, has significance for coupling with carbon capture via the reaction scheme presented in figure 13²¹¹. Worldwide, acrylic acid demand is high (3 Mt/y) and projected to increase at 4% per annum; its most common application is in plastics production (e.g. for coatings, adhesives, elastomers, floor polishes and paints)²¹².

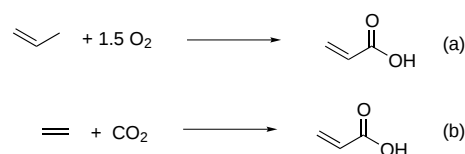


Fig. 13 Propylene oxidation process (a) vs CO₂-ethylene route (b) towards the synthesis of acrylic

Another way to view carbon dioxide chemistry is through the cleavage of one C-O bond to generate one equivalent of carbon monoxide and a reactive oxo group that can be transferred to an organic residue. Carbon dioxide can therefore be regarded as a safe oxidant of low toxicity. However, only a limited number of such oxo transfer reactions have been described. Firstly the oxo function can be directly transferred to the metal center through an oxidation process, in early transition metals^{213,214} or it can react via metathesis reactions with a carbene or an imido complex to yield isocyanates or esters^{215,216}. Carbon dioxide has also been envisaged as a hydroformyl source under high pressure of dihydrogen (via formation of carbon monoxide through the reverse gas shift reaction $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$) and a handful of hydroformylation reactions of alkenes has been reported to date²¹⁷.

3.2.2 Fuels and C-1 molecules

Fossil fuels are currently our primary energy resource and moreover provide key raw materials for the chemicals industry. The catalytic conversion of CO₂ to liquid fuels is a worthwhile goal that would positively impact the global carbon balance by recycling CO₂ into usable fuels. The energetics of CO₂ activation suggests only very few target molecules as viable, including methanol, formic acid and methane (see table 3).

Reducing agents are required to carry out this activation; these can take the form of gaseous hydrogen or protons and electrons. The general reduction reaction for CO₂ activation can be expressed as in equation (14):

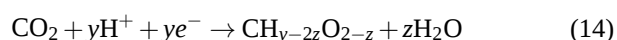


Table 3 CO₂ reduction reactions to liquid or gaseous carbon based fuel (ΔE° and ΔG° values are for 298 K)

Reaction	ΔE° (V)	ΔG° (kJmol ⁻¹)
H ₂ O → H ₂ + $\frac{1}{2}$ O ₂	1.23	56.7
CO ₂ + H ₂ → HCOOH	-	5.1
CO ₂ + H ₂ O → HCOOH + $\frac{1}{2}$ O ₂	1.34	61.8
CO ₂ + H ₂ → CO + H ₂ O†	-	4.6
CO ₂ → CO + $\frac{1}{2}$ O ₂	1.33	61.3
CO ₂ + 3H ₂ → CH ₃ OH + H ₂ O	-	-4.1
CO ₂ + 2H ₂ O → CH ₃ OH + $\frac{3}{2}$ O ₂	1.20	166
CO ₂ + 4H ₂ → CH ₄ + 2 H ₂ O	-	-31.3
CO ₂ + → CH ₄ + 2O ₂	1.06	195

† Note that this is the reverse water-gas shift reaction

For production of formic acid: $y = 2$, $z = 0$; methanol: $y = 6$, $z = 1$; methane: $y = 8$, $z = 2$.

Strategically, there are two ways that the use of carbon dioxide to make fuels can be accomplished. The first is to convert CO₂ and H₂O into CO and H₂ (syn gas), and then to use well proven Fischer-Tröpsch technologies to convert the synthesis gas to liquid fuels, including gasoline. The advantage here is that it is considerably easier to convert CO₂ to CO and H₂O to H₂ than it is to make even a simple liquid fuel such as methanol by electrocatalytic processes. The second option is to directly convert CO₂ to liquid fuels. Here, the kinetic challenges are great. One possibility is to identify a single catalyst that can direct the complete sequence of steps necessary for converting CO₂ to CO, to H₂CO, to hydrocarbons or alcohols, all with low kinetic barriers. Three routes have been examined for creating and utilising reducing agents in the activation/transformation of CO₂: the direct reduction by dihydrogen, the electrochemical reduction, and the photochemical reduction.

The thermochemical CO₂ reduction (CO₂ hydrogenation) is already present in industrial processes. Indeed, methanol is currently produced using the ICI/Synetix process on a scale of 25 Mt/yr worldwide, which uses a multi-component metal oxide catalyst (Cu/ZnO/Alumina) and syn gas²¹⁸. For this process, the CO₂ is used as an component of a syn gas (CO₂ (8%)/CO (13%)/H₂ (72%)) mixture made from natural gas, although it is important to note that it is the CO₂ (and not the CO) in the mixture which is transformed into the methanol. However, currently the production of methanol by the thermochemical reduction of CO₂ still consumes too much hydrogen and thermal energy to have a positive impact on carbon dioxide emissions. In order to decrease the required thermal energy input, improved catalysts are therefore required, enabling less forcing conditions to be used. This is particularly important in a process context as lower temperatures will res-

ult in higher methanol yields owing to a lessening of the equilibrium constraint. Two important developments are notable in this regard: 1) the conversion of CO₂ into methanol using silanes, using N-Heterocyclic carbene catalysts, at room temperature²¹⁹ and 2) the stoichiometric reduction of CO₂ to methanol at very low pressures of hydrogen (1-2 atm) using hindered organocatalysts (frustrated Lewis pairs)²²⁰. Several homogeneous metallic catalysts are also now known for the hydrogenation of CO₂ to formic acid^{195,221,222}.

Direct electrochemical reduction of carbon dioxide on most electrode surfaces requires large overvoltages which consequently lowers the conversion efficiency. The homogeneous electrochemical reduction of carbon dioxide therefore requires catalysts able to increase the electron transfer and chemical kinetics of the reduction process. Ideally, the electrocatalyst must match the redox potential for the electron transfer with the chemical reaction (i.e.. reduction of CO₂ to CO) and thereby only require a low overvoltage. A variety of late transition metal complexes, stabilized by macrocyclic ligands, have been shown to be active for these processes¹⁹¹. In 2002²²³, it was for example reported by Ishida and co-workers that bipyridine complexes of ruthenium could catalyze the reduction of CO₂. [Ru(bipy)(CO)₂]²⁺ and [Ru(bipy)(CO)Cl]⁺ were found to electrocatalytically reduce CO₂ to CO, H₂, and HCOO⁻ at 1.40 V vs. SCE.

Finally, photochemical systems have also been studied in an effort to develop systems capable of directly reducing CO₂ to fuels or chemicals using solar energy^{224,225}. Transition-metal complexes have been used as both catalysts and solar energy converters, since they can absorb a significant portion of the solar spectrum, have long-lived excited states, and are able to promote the activation of small molecules. Cobalt complexes with N- macrocyclic ligands and [Ru(bipy)₂(CO)_Xn] complexes ($X = \text{CO}, \text{Cl}, \text{H}$) have shown interesting activity²²⁴. Photochemical CO₂ reduction catalysis has been carried out under 1.0 atm CO₂ at room temperature using water as the source of electrons²²⁶. However, the activity of these photochemical systems are still very low and, furthermore, they require low catalyst concentrations. As yet this field is still in its infancy and improvements can be expected.

3.2.3 CO₂ derived plastics

In 1969, Inoue reported the zinc catalysed sequential copolymerisation of carbon dioxide and epoxides into polycarbonates²²⁷. The catalyst used was an ill-defined zinc alkoxide aggregate formed by mixing dialkyl zinc reagents and alcohols. Since then, the copolymerisation of CO₂ with epoxides has received much attention, with the reaction scheme being illustrated in figure 14^{228,229}. This process provides a sustainable route to polycarbonates compared to the established commercial syntheses, via polycondensation reactions between phos-

gene (a highly toxic, corrosive, nerve gas) and diols in copious amounts of methylene chloride, or by transesterification processes of cyclic carbonate with diols (e.g. bisphenol-A). To a lesser extent the synthesis of polyurethanes from supercritical CO₂ and aziridines has also been investigated²³⁰.

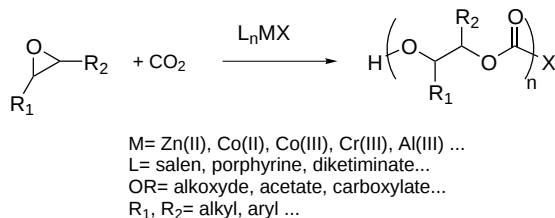


Fig. 14 General scheme of CO₂/epoxides copolymerisation

Polycarbonates are currently produced on a 4 Mt/y scale²³¹ and are thermosetting polymers with physical properties amenable to bulk processing and a wide range of applications. The polycarbonate derived from bisphenol A is the major industrial product. Currently, various aliphatic polycarbonates can be produced by the sequential copolymerisation of CO₂ and epoxides.^{232,233} These aliphatic polyesters may go some way to satisfying a growing consumer demand for sustainably produced construction materials and packaging materials. There is also scope for the development of new polymers and composites to improve the thermo-mechanical properties of the aliphatic polycarbonates and impact aromatic (BPA) polycarbonate applications.

Since Inoue's initial discovery, the research field has been thoroughly explored from a synthetic and mechanistic point of view²³⁴, and chromium, cobalt, zinc and aluminum alkoxide, halide and acetate complexes have proven very effective^{235–239}. Some lanthanide complexes were also found to be viable catalysts^{240,241}. Yet, the alternating copolymerisation of carbon dioxide with epoxides is still one step away from commercialisation, despite the report of some systems active at low CO₂ pressure^{234,242,243}. The major factor preventing application of this technology is the low catalytic activity. Improvement of the known catalytic systems or discovery of new catalysts is therefore desirable. For the past decades, the quest for well-defined catalysts has focused on single site metal complexes, where a bulky ancillary ligand prevents aggregation (i.e. L_nMOR where L_n: ancillary ligand(s), M: Lewis acidic metal, e.g. Zn(II), OR: alkoxide/acetate group to initiate the polymerisation)²⁴³. Yet there have been clues in the literature, even since the 1970s, that the mechanism may involve two metal centres cooperating with each other or a bimetallic active site^{195,202}. According to this proposal one metal binds and activates the epoxide whilst the other metal attacks the epoxide using a bound alkoxide/carboxylate/carbonate group.

Some of the authors recently reported the activity of a series of very active bimetallic zinc catalyst, with a reduced Robsons macrocyclic ancillary ligand^{243,244}. The catalyst presented in figure 15 is one of only a few active at 1 atm CO₂, with turn-over-numbers up to 700 and turn-over-frequencies of 30h⁻¹. This catalyst has also the advantage of being air stable, robust and able to polymerise unpurified (i.e. wet) cyclohexene oxide with no loss of activity.

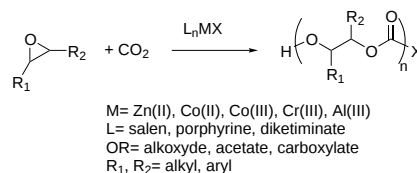


Fig. 15 General scheme of CO₂/epoxides copolymerisation

Finally, to date, only limited studies have addressed the copolymerisation of carbon dioxide and epoxides other than cyclohexene oxide/propylene oxide. Therefore, the range of materials that can be prepared using this method is somewhat limited. To widen the range of potential applications, the quest for well-defined efficient catalysts that will enable the copolymerisation of CO₂ with other monomers (substituted epoxides or vinyl ethers) is on-going.

3.2.4 Outlook

Current commercial processes only use 120 Mt of CO₂ per year for chemicals manufacture, whilst the annual CO₂ emissions of a single power plant exceed 4 Gt! In the short term, therefore, it is clear that transforming CO₂ to products will not significantly impact global CO₂ concentrations. However, chemicals produced using CO₂ as the feedstock can provide a significant economic stimulus for carbon capture and transformation. The target products in such a scenario need to have established markets and therefore replacing petrochemical feedstocks with CO₂ is the primary goal. In the medium to long term, research efforts must focus on the reduction of carbon dioxide to liquid fuels, finding sustainable methods to produce liquid transport fuels is a key challenge for the next fifty years. In parallel with these research efforts devoted to renewable transport fuels, attention should also be paid to using CO₂ to produce new products and materials, for example polymers. Such new materials will meet the demands of emerging markets, for example for sustainable packaging and construction materials, and need not be seen as simply displacing conventional petrochemicals. In conclusion, there is clearly an urgent desire to develop versatile and efficient processes for the conversion of CO₂ into new and known products to provide economic stimulus for CO₂ capture and in the longer

term to have a positive impact on the greenhouse gas concentrations/emissions.

4 Multiscale process systems engineering and carbon capture and storage

4.1 Multiscale systems models and CCS

A multiscale modelling approach is becoming the methodology of choice to describe a complex system that exhibits behaviour across length and time scales with many orders of magnitude^{245,246}

This exploits a series of interacting, scale-specific models (see figure 16). Early applications of this approach to systems such as polymerisation and bioprocessing have proven that multiscale modelling is rightly regarded as a promising and powerful tool in various disciplines. There is enormous scope for the application of this approach to the emerging area of CCS system design and operation. The potential roles for multiscale process systems modelling in CCS include:

- The design and optimisation of carbon capture processes
- Carbon capture process integration: steady state
- Carbon capture process integration: dynamics and operability
- Network design and operability analysis

Each of these areas is reviewed briefly below.

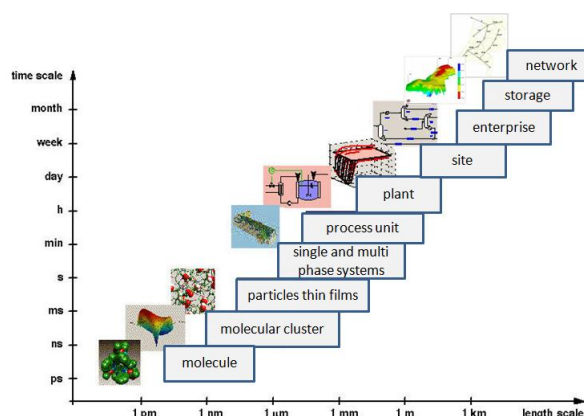


Fig. 16 Illustration of multiscale modelling

4.2 Capture process design and optimisation

Different carbon capture processes have been described in great detail in the sections above. Multiscale modelling is very

useful in understanding and exploiting the important rate processes that drive the carbon capture process. For example, in amine absorption, it is critical to understand the rate limiting processes governing the transfer of CO₂ between phases to ensure that the equipment is correctly sized. Sophisticated mass transfer based models for the design and operational analysis of absorbers have been developed by Kvamsdal *et al.*²⁴⁷ who were able to simulate process start-up and by Lawal *et al.*²⁴⁸ who compared equilibrium-based and rate-based approaches and found that the latter gave more accurate model predictions.

These detailed models can be used to estimate the capital costs and energy requirements as a function of capture extent and flue gas CO₂ concentration. At the stage of equipment design, it might be best to establish the costs and energy requirements as functions of these performance parameters; this is because it will not be clear what values are “optimal” until the rest of the system and its infrastructure are examined. Similarly, the solid looping family of processes can also benefit from model-based design. Here, the rate processes are even more complex, involving gas phase mass transfer, pore and ash layer diffusion and chemical reaction. The situation is further complicated by a distribution of particle lifetimes in the system. Nevertheless, a multiscale model can be used to determine optimal design parameters (residence times, temperatures, equipment geometries, particle replacement rates etc.). A relatively simple model of the carbonate looping process was developed by Strohle *et al.*²⁴⁹ who demonstrated that this approach should be more efficient than solvent-based absorption. Detailed models tend to focus on particle level phenomena and should ultimately be integrated with unit-level and process-level models in a multi-scale fashion to support optimised process design²⁵⁰.

4.3 Process integration: steady state operation

Process integration seeks to identify opportunities to couple process and sub-processes, in particular through the cascading of heat from higher to lower duties. It has been successfully applied to an enormous number of process industry systems over the past three decades²⁵¹.

In the context of carbon capture, the main opportunity for process integration is in the use of heat at the appropriate temperature to support solvent regeneration (stripping) processes. This comes about from integrated modelling of the power plant and the capture plant and identifies opportunities for energy integration between them. Oexmann and Kather^{50,252} point out that much solvent screening and attempted optimisation of carbon capture processes focuses only on identifying solvents with a low heat of absorption when in fact it is better to try to optimise the whole system including the power plant thermodynamics.

Galindo Cifre *et al.*²⁵³ develop an integrated mathematical model of a power plant and an amine-based carbon capture plant with a view to minimising the efficiency losses via energy integration. They start with the conventional assumption that up to 2/3 of the steam from between the intermediate pressure and low pressure turbine sections is used to provide heat for the solvent. Using BASFs CHEMASIM model to describe the important processes in the carbon capture system and EBILSON for the power plant, they were able to manipulate the stripper operating pressure, the solvent type and recirculation rate and the absorber height to optimise the integrated system. The optimised cases demonstrated reductions in efficiency losses of between 1% and 5%.

Harkin *et al.*²⁵⁴ perform a similar analysis using the pinch method driven by simulation data from the power plant and capture plant. A pulverised brown coal power plant was used as the base case. Options included no energy integration, maximum energy integration with different heat exchanger minimum approach temperatures and the latter with coal drying. It was found that effective whole process integration strategies can reduce the energy penalty from 39% to 24%.

4.4 Process integration: dynamics and operability

The studies described above employ “steady-state models which aim to generate designs that perform well at nominal, average operating conditions. Another important aspect of process integration between power plant and capture plant relates to dynamic operations and operability analysis, aiming to understand issues such as whether the capture plant compromises the power plants ability to ramp up or down or whether the part load efficiency is different from that at the nominal operating conditions. This requires the development of dynamic models which capture the transient performance of the carbon capture plant.

Chalmers *et al.*²⁵⁵ list the following modes of flexibility required from the integrated system:

- Quick start-up/shut-down: required for plants that are required to respond quickly to changes in power demand. In the UK grid code for example, the most stringent requirement is being able to change load 10% in 10 seconds, necessary if plants have bid to operate in frequency response mode.
- Quick change in output: similarly required for plants required to respond quickly, especially while other plants start-up
- Effective operation at part load: for plants that only run at higher loads when required
- Increase in maximum output: for very fast response, e.g. by using stored steam or by bypassing carbon capture for

short periods

- Decrease in minimum output: for plants that must be kept running even at times of very low power demand
- Ability to use different fuels (e.g. co-firing with biomass)
- By-pass of capture plant to allow the power plant to operate under fault conditions in the capture plant

In order to evaluate the above for a fixed design, or to improve the operability of proposed designs, dynamic models of the power plant and capture plant are required. The level of detail required for such models is still the subject of much debate. Chalmers *et al.*²⁵⁵ argue that designing the integration strategy around maximum efficiency at full load may compromise dynamic flexibility. They focus their work on achievable system ramp rates and describe a number of strategies around capture plant operation (e.g. solvent storage, temporary by-passing) which should result in minimal compromises to power plant ramp rates. There are however, concerns arising from changing CO₂ stream compositions during transients and their effects on downstream compression, transport and injection.

4.5 Network design and analysis

The final area of interest to systems modellers is the whole system of carbon dioxide production, capture, transportation, injection and storage. A system-wide analysis of this “CCS infrastructure is very useful in helping to answer a number of strategic questions, including:

- How should the network evolve over time? Does it make sense to allow many single point-to-point system early on or provide an (oversized) backbone early on which pays off in the long term?
- What are the important system integration issues associated with the interfaces between different components of the infrastructure (e.g., how do impurities in captured CO₂ affect the phase behaviour and therefore pipeline operation)?
- What is the expected overall system cost and how does it vary with increasing carbon reduction targets?
- What are the other important system-wide metrics (e.g. environmental impact, safety, operability and how should they be evaluated? Are there any trade-offs between system-wide metrics?
- How should sensible early stage decisions be made given the large future uncertainties around costs and regulations?

Much can be learned from the literature on large scale infrastructure investments, where infrastructure development is staged over time and subject to future uncertainties. Early work in this area includes a deterministic optimisation model to design value chains for Norway²⁵⁶ and the United Arab Emirates²⁵⁷. In both cases, a mathematical model is used to connect sources and sinks, design pipelines and establish CO₂ flowrates in the network and evaluate system costs. Similarly, life cycle analyses have been performed to evaluate overall environmental impacts of fixed CCS system infrastructures^{258,259}.

More sophisticated techniques will need to use optimisation under uncertainty. Two useful approaches in this field are multistage stochastic optimisation and real options. In both cases the key concept is that early stage decisions must be firm while future decisions are contingent on new information available in the future and do not need to be committed immediately. The link between the firm early stage decisions and the uncertainty dependent future decisions ensures that the early stage decisions are robust with respect to future outcomes. An example of this approach²⁶⁰ considers the use of real options rather than standard discounted cash flow models to determine if and when to invest in different technological options.

5 Conclusions

Worldwide, research is being performed to abate global climate change, which a consensus of the scientific community indicates is due, at least in part, to anthropogenic GHG emissions². CO₂ capture and separation from large fixed-point emission-sources, such as power-plants, can be achieved through continued research, development, and demonstration. A wide range of technologies exist to facilitate the large scale capture, transport and storage of CO₂. Many of these technologies are already being used in commercial plants, particularly in the chemical industry, but scale-up is needed to match the sizes of large modern power plants. Large-scale integrated operation of power generation, CO₂ capture, transmission, and storage needs to be demonstrated to increase investor and public confidence in the technology and to reduce costs by “learning by doing”. In this contribution, we have critically assessed three of the most promising technologies that are deemed suitable for near to medium term deployment in large scale CCS applications.

The main advantages and disadvantages of the CO₂ capture technologies reviewed - including an evaluation of the maturity of the technologies - are summarised in table 5. In order to evaluate the maturity of the technologies, we used a ranking scale from 1-9, known as the technology readiness levels (TRLs). This scale, which was developed by NASA, is useful for evaluating emerging energy technologies that are at very different stages of development, and it has previously been

adopted by the UK Advanced Power Generation Technology Forum (UK APGF)²⁶¹. A summary of the technology readiness levels is presented in Table 4 and justification for the selected TRLs is given on the basis of our up-to-date review of the technologies, as well as the status of demonstration projects planned and/or underway. A further observation that may be drawn from the exercise of ranking these technologies is the likely timeframe for a technology to advance from applied and strategic research to technology- and system-validation. For example, post-combustion carbonate looping has progressed from bench-scale (TRL: 1-2) to a planned demonstration at 1 MW (TRL:4-5) in only 5-10 years. It must be acknowledged that the final deployment of the technology is generally considered the most risky stage of development due to the potential to underestimate the actual costs⁶⁰.

Based on current technology, it is estimated that CCS would significantly reduce the net efficiency of existing power-plants. Costs are expected to be higher for the initial deployment of this technology, but both economic and energy penalties are expected to reduce with time as the systems and practices associated with CCS processes evolve. Wide deployment of these technologies is necessary to mitigate GHG emissions and ultimately achieve climate stabilization. It is anticipated that the net cost of power generation with CCS will eventually be lower than the cost of unabated generation because the cost of buying CO₂ emission permits will be avoided. This, however assumes sufficient political will to create an economic landscape in which this environment can thrive.

Table 4 Technology readiness levels (TRL), adapted by the UK Advanced Power Generation Technology Forum²⁶¹

TRL	Status
	Applied and strategic research
1	Basic principles observed and reported
2	Technology concept and/or application formulated
3	Analytical and experimental critical function and/or characteristic proof of concept
4	Technology / part of technology validation in a laboratory environment
	Technology validation
5	Technology / part of technology validation in a working environment
6	Technology model or prototype demonstration in a working environment
	System validation
7	Full-scale technology demonstration in working environment
8	Technology completed and ready for deployment through test and demonstration
9	Technology deployed

Table 5 Summary of CO₂ capture technologies including the authors ranking according to technology readiness levels

Technology	Advantages	Technical challenges
Chemisorption (TRL = 6)	Very well-known technology, deployed on large-scale across several industries, suitable for retrofit.	Significant energy penalty associated with solvent regeneration, and the solvents used are susceptible to degradation in the presence of other acid gases and oxygen. Capital and operating costs as well as deleterious environmental impacts associated with fugitive solvent emissions must be reduced
Carbonate looping (TRL = 4-5)	Very well-known technology, deployed on large-scale across several industries, suitable for retrofit. Moreover this technology uses a very cheap and abundant sorbent (limestone). There is an important synergy with the cement industry.	The sorbent is vulnerable to decay in capture capacity (though, still to a relatively high capacity compared to many sorbents), and competing reactions cause chemical deactivation. This technology must be demonstrated at large scale, under industrially relevant conditions.
Oxy-fuel (TRL = 5)	Relatively simple technology, suitable for retrofit. This process forms significantly less NO _x than comparable CCS processes.	Significant energy penalty associated with the separation of O ₂ from N ₂ . There is the potential for relatively high corrosion rates due to elevated CO ₂ and SO ₂ concentrations.

6 Acknowledgements

N.M.D thanks the British Coal Utilisation and Research Association (BCURA) for the funding of a PhD studentship, BCURA B82. Financial support from the Engineering and Physical Sciences Research Council (EPSRC) of the UK (Grant number: EP/E016340/1) to the Molecular Systems Engineering group is also acknowledged. P.S.F. thanks Doosan Babcock for permission to reproduce figures 4 and 5 in this paper.

References

- 1 IPCC, *Intergovernmental Panel on Climate Change, Third Assessment Report*, Ipc technical report, 2001.
- 2 B. Metz, O. Davidson, H. C. de Coninck, M. Loos and L. A. Meyer, *IPCC, 2006: IPCC Special Report of Carbon Dioxide Capture and Storage. Prepared by Working Group III of the Intergovernmental Panel on Climate Change*, Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 2005.
- 3 *Meeting the energy challenge: A white paper on energy*, Department of trade and industry technical report, 2007.
- 4 E. A. Parson and D. W. Keith, *Science*, 1998, **282**, 1053–1054.
- 5 P. S. Newall, S. J. Clarke, H. Scholes, N. R. Clarke, P. A. King and R. W. Barley, *CO₂ storage as carbonate minerals*, Iea greenhouse gas r&d program technical report, 2000.
- 6 J. Blamey, E. J. Anthony, J. Wang and P. S. Fennell, *Prog. Energy. Combust.*, 2010, **36**, 260–279.
- 7 M. H. de Brito, U. von Stockar, A. M. Bangerter, P. Bomio and M. Laso, *Ind. Eng. Chem. Res.*, 1994, **33**, 647–656.
- 8 H. Chalmers and J. Gibbins, *Fuel*, 2007, **86**, 2109–2123.
- 9 H. Herzog, *The Capture, Utilization and Disposal of Carbon Dioxide from Fossil Fuel-Fired Power Plants*, Department of Energy Technical Report DOE/ER-30194, 1993.
- 10 R. Barchas and R. Davis, *Energy Conversion and Management*, 1992, **33**, 333–340.
- 11 M. T. Sander and C. L. Mariz, *Energy Convers. Mgmt.*, 1992, **33**, 341–348.
- 12 Recovery of CO₂ from flue gases: Commercial trends, 1999.
- 13 T. Mimura, S. Shimojo, T. Suda, M. Ijima and S. Mitsuoka, *Energy Convers. Mgmt.*, 1995, **36**, 397–400.
- 14 D. W. Bailey and P. H. M. Feron, *Oil Gas Sci. Technol.*, 2005, **60**, 461–474.
- 15 A. L. Kohl and F. C. Riesenfeld, *Gas Purification*, Gulf Publishing Company, Houston, Texas, Houston, Second edn, 1974.
- 16 D. S. Arnold, D. A. Barrett and R. H. Isom, *Oil and Gas Journal*, 1982, **80**, 130–136.
- 17 S. Reddy, J. Scherffius, S. Freguia and C. Rioberts, In *Proceedings of the 2nd Annual Conference on Carbon Sequestration*, Alexandria, Virginia, USA, 2004.
- 18 S. M. Murphy, A. Sorooshian, J. H. Kroll, N. L. Ng, P. Chhabra, C. Tong, J. D. Surratt, E. Knipping, R. C. Flagan and J. H. Seinfeld, *Atmos. Chem. Phys.*, 2007, **7**, 2313–2337.
- 19 Q. G. J. Malloy, L. Qi, B. Warren, D. R. Cocker, M. E. Erupe and P. J. Silva, *Atmos. Chem. Phys.*, 2009, **9**, 2051–2060.
- 20 G. Astarita, *Mass Transfer With Chemical Reaction*, Elsevier, London, 1967.
- 21 H. Hikita, S. Asai, H. Ishikawa and M. Honda, *Chem. Eng. J.*, 1977, **13**, 7–12.
- 22 P. V. Danckwerts, *Chem. Eng. Sci.*, 1979, **34**, 443–446.
- 23 S. S. Laddha and P. V. Danckwerts, *Chem. Eng. Sci.*, 1981, **36**, 479–482.
- 24 D. E. Penny and T. J. Ritter, *J. Chem. Soc., Faraday Trans. I.*, 1983, **79**, 2103–2109.
- 25 P. M. M. Blauwhoff, G. F. Versteeg and W. P. M. van Swaaij, *Chem. Eng. Sci.*, 1984, **39**, 207–225.
- 26 G. Sartori, W. A. Ho, W. A. Thaler, G. R. Chludzinski and J. C. Wilbur, in *Carbon dioxide chemistry: Environmental issues*, Royal Society of Chemistry, Cambridge, UK, 1994, ch. Sterically hindered amines for acid gas absorption.
- 27 M. Edali, A. Aboudheir and R. Idem, *Int. J. of Greenh. Gas Con.*, 2009, **3**, 550–560.
- 28 M. L. Kennard and A. Meisen, *Hydrocarbon Process., Int. Ed.*, 1982, **59**, 103–106.
- 29 A. Chakma and A. Meisen, *J. Chromatogr. A.*, 1988, **457**, 287–297.
- 30 A. Chakama and A. Meisen, *Can. J. Chem. Eng.*, 1997, **75**, 861–871.
- 31 A. Bello and R. O. Idem, *Ind. Eng. Chem. Res.*, 2006, **45**, 2569–2579.
- 32 T. Supap, R. Idem, P. Tontiwachwuthikul and C. Saiwan, *Ind. Eng. Chem. Res.*, 2006, **45**, 2437–2451.
- 33 J. Critchfield and J. Jenkins, *Pet. Technol. Q.*, 1999, 87.
- 34 G. Astarita, D. W. Savage and A. Biso, *Gas Treating With Chemical Solvents*, John Wiley and Sons, New York, 1983.
- 35 B. R. Strazisar, R. R. Anderson and C. M. White, *Degradation of mono-ethanolamine used in carbon dioxide capture from flue gas of a coal fired electric power generating station*, National energy technology laboratory technical report, 2006.
- 36 A. Meisen and X. Shuai, *Energy Conserv. Mgmt.*, 1997, **38**, S37–S42.
- 37 Introduction to sulphur chemistry and sulphur handling, Barcelona, Spain, 2004.
- 38 H. Lepaumier, D. Picq and P. L. Carrette, *Ind. Eng. Chem. Res.*, 2009, **48**, 9061–9067.
- 39 P. C. Rooney, T. R. Bacon and M. S. Dupart, *Hydrocarbon Process., Int. Ed.*, 1996, **75**, 95.
- 40 P. C. Rooney, M. S. DuPart and T. R. Bacon, *Pet. Technol. Q.*, 1998, **97**, 101.
- 41 *Improvement in Power Generation with Post-Combustion Capture of CO₂, Report PH4/33*, Iea ghg technical report, 2004.
- 42 P. Jackson and M. Atalla, *Int. J. Greenhouse. Con.*, 2010.
- 43 J. J. Renard, S. E. Calidonna and M. V. Henley, *J. Hazardous Mater.*, 2004, **108**, 29–60.
- 44 M. Attalla, The 5th Trondheim conference on CO₂ capture, transport and storage, 2009.
- 45 N. Kladkaew, R. Idem., P. Tontiwachwuthikul and C. Saiwan, *Ind. Eng. Chem. Res.*, 2009, **48**, 10169–10179.
- 46 R. R. Bottoms, (Girdler Corp.), *Separating acid gases*, 1930, U. S. Patent 1783901.
- 47 H. Bosch, G. F. Gersteeg and W. P. M. Van Swaaij, *Chem. Eng. Sci.*, 1989, **44**, 2745–2750.
- 48 G. Sartori and D. W. Savage, *Ind. Eng. Chem. Fundam.*, 1983, **22**, 239–249.
- 49 G. Sartori, W. S. Ho, D. W. Savage, G. R. Chludzinski and S. Wlechert, *Sep. and Purif. Rev.*, 1987, **16**, 171–200.
- 50 J. Oexmann and A. Kather, *Int. J. Greenh. Gas Con.*, 2010, **4**, 36–43.
- 51 P. Tontiwachwuthikul, A. Meisen and L. C. J., *Chem. Eng. Sci.*, 1992, **47**, 381–390.
- 52 J. Gabrielsen, M. L. Michelsen, E. H. Stenby and G. M. Kontogeorgis, *Ind. Eng. Chem. Res.*, 2005, **44**, 3348–3354.
- 53 J. Gabrielsen, M. L. Michelsen, E. H. Stenby and G. M. Kontogeorgis, *AIChE J.*, 2006, **52**, 3443–3451.
- 54 J. Gabrielsen, H. F. Svendsen, M. L. Michelsen, E. H. Stenby and G. M. Kontogeorgis, *Chem. Eng. Sci.*, 2007, **62**, 2397–2413.
- 55 F. A. Tobiesen, H. F. Svendsen and O. Juliussen, *AIChE J.*, 2007, **53**, 846–865.
- 56 A. K. Chakraborty, A. Astarita and K. B. Bischoff, *Chem. Eng. Sci.*, 1986, **41**, 997–1003.
- 57 J. K. You, H. Park, S. H. Yang, W. H. Hong, W. Shin, J. K. Kang, K. B. Yi and J. N. Kim, *J. Phys. Chem. B*, 2008, **112**, 4323–4328.
- 58 T. S. Mimura, M. Iijima and S. Mitsuoka, 4th International Conference on Greenhouse Gas Control Technologies, 1988, pp. 71–76.
- 59 T. Mimura, S. Satsumi, M. Iijima and S. Mitsuoka, 4th International Conference on Greenhouse Gas Control Technologies, 1998.
- 60 J. Davison and K. Thambimuthu, *Proc. IMechE*, 2009, **223**, 201–212.
- 61 H. Bai, P. Biswas and T. Keener, *Ind. Eng. Chem. Res.*, 1994, **33**, 1231–1236.
- 62 H. Bai and A. C. Yeh, *Ind. Eng. Chem. Res.*, 1997, **36**, 2490–2493.
- 63 A. C. Yeh and B. Hsunling, *Sci. Tot. Environ.*, 1999, **228**, 121–133.
- 64 K. P. Resnik, J. T. Yeh and H. W. Pennline, *Int. J. Env. Tech. Mgmt.*,

- 2004, **4**, 89–104.
- 65 H. Lepaumier, D. Picq and P. L. Carrette, *Ind. Eng. Chem. Res.*, 2009, **48**, 9068–9075.
- 66 Alstom, *Mod. Power Syst.*, 2006, **26**, 17–18.
- 67 R. Peltier, *Alstom's chilled ammonia CO₂ capture process advances toward commercialisation*, 2008, Available from: www.powermag.com.
- 68 J. D. Figueroa, T. Fout, S. Plasynski and H. McIlvried, *Int. J. Greenh. Gas Ctrl.*, 2008, **2**, 9–20.
- 69 B. P. Mandal, M. Guha, A. K. Biswas and S. S. Bandyopadhyay, *Chem. Eng. Sci.*, 2001, **56**, 6217–6224.
- 70 B. P. Mandal and S. S. Bandyopadhyay, *Chem. Eng. Sci.*, 2006, **61**, 5440–5447.
- 71 A. Setameteekul, A. Aroonwilas and A. Veawab, *Sep. and Purif. Tech.*, 2008, **64**, 16–25.
- 72 M. Nainar and A. Veawab, *Energy Procedia*, 2009, **1**, 231–235.
- 73 A. Dey and A. Aroonwilas, *Energy Procedia*, 2009, **1**, 211–215.
- 74 A. Aroonwilas and A. Veawab, *Energy Procedia*, 2009, **1**, 4315–4321.
- 75 R. Sakwattanapong, A. Aroonwilas and A. Veawab, *Energy Procedia*, 2009, **1**, 217–224.
- 76 W. J. Choi, J. B. Seo, S. Y. Jang, J. H. Jung and W. J. Oh, *J. Env. Sci.*, 2009, **21**, 907–913.
- 77 W. J. Choi, B. M. Min, B. H. Shon, J. B. Seo and K. J. Oh, *J. Ind. Eng. Chem.*, 2009, **15**, 635–640.
- 78 D. H. Lee, W. J. Choi, S. J. Moon, S. H. Ha, I. G. Kim and K. J. Oh, *Korean J. Chem. Eng.*, 2008, **25**, 279–284.
- 79 A. Archane, L. Gicques, E. Provost and W. Fürst, *Chem. Eng. Res. Des.*, 2008, **86**, 592–599.
- 80 R. Process, Available From: www.linde.com/process_plants/hydrogen_syngas_plants/gasprocessing/rectisol_wash.php.
- 81 A. C. Larsson, The 5th Trondheim conference on CO₂ capture, transport and storage, 2009.
- 82 E. S. Rubin and A. B. Rao, *A technical, economic and environmental assessment of amine-based CO₂ capture technology for power plant greenhouse gas control*, National Energy Technology Laboratory Technical Report DE-FC26-00NT40935, 2001.
- 83 N. Holt, 2nd IGCC and XtL Conference, Freiberg, Germany, 2007.
- 84 E. S. Rubin, S. Yeh, M. Antes, M. Berkenpas and J. Davison, *Int. J. Greenh. Gas Con.*, 2007, **1**, 188–197.
- 85 <http://www.co2cesar.eu/site/en/about.php>.
- 86 Calcium Looping Research at Imperial College, London, 2009.
- 87 J. C. Abanades, E. J. Anthony, J. Wang and J. E. Oakey, *Environ. Sci. and Tech.*, 2004, **39**, 2861–2866.
- 88 B. Balasubramanian, A. Lopez Ortiz, S. Kaytakoglu and D. P. Harrison, *Chem. Eng. Sci.*, 1999, **54**, 3543–3552.
- 89 R. Barker, *J. App. Chem. and Biotechnol.*, 1973, **24**, 221–227.
- 90 H. Ziock, E. L. Brosha, F. H. Garzon, G. D. Guthrie, A. A. Johnson, A. Kramer, K. S. Lackner, F. Lau, R. Mukundan, M. Nawaz, T. W. Robison, B. Roop, J. Ruby, B. F. Smith and J. Wang, *Technical progress in the development of zero emission coal technologies*, technical report, 2003.
- 91 T. E. T. P. for Zero Emission Fossil Fuel Power Plants, *Recommendations for RTD, support actions and international collaboration activities within FP7 Energy Work programmes in support of deployment of CCS in Europe*, technical report, 2008.
- 92 D. Y. Lu, R. W. Hughes and E. J. Anthony, *Fuel Proc. Tech.*, 2008, **89**, 1386–1395.
- 93 J. C. Abanades, M. Alonso, N. Rodriguez, B. Gonzalez, F. Fuentes, G. Grasa and M. R., In-Situ Carbon Removal 4. Imperial College, London, 2008.
- 94 O. Masek, A. Bosoaga and J. Oakey, In-Situ Carbon Removal 4. Imperial College, 2008.
- 95 C. Hawthorne, A. Charitos, C. A. Perez-Pulido, Z. Bing and S. G., 9th International Conference on Circulating Fluidized Beds. Hamburg, Germany, 2008.
- 96 A. Charitos, C. Hawthorne, A. Bidwe, L. He and G. Scheffknecht, 9th International Conference on Circulating Fluidized Beds. Hamburg, Germany, 2008.
- 97 Spanish language press releases available from <http://cienciatec.wordpress.com> and <http://www.lne.es>.
- 98 J. Strohle, A. Galloy and B. Epple, *Energy Procedia*, 2009, **1**, 1313–1320.
- 99 L. S. Fan, G. dastidar A. and S. Mahuli, US Patent Application 08/584089. USA. 1998.
- 100 A. Roder, *CEMEX Climate Change Strategy and CCS*, Imperial college, london, uk. technical report, 2008.
- 101 McKinsey, *Greenhouse gas abatement cost curves*, www.mckinsey.com/clientservice/ccsi/Costcurves.asp.
- 102 R. H. Borgwardt, *Chem. Eng. Sci.*, 1989, **44**, 53–60.
- 103 J. J. Saastamoinen, *Ind. Eng. Chem. Res.*, 2007, **46**, 7308–7316.
- 104 E. J. Anthony and D. L. Granatstein, *Prog. Energ. Combust.*, 2001, **27**, 215–236.
- 105 Z. X. Chen, J. R. Grace and C. J. Lim, *Chem. Eng. Sci.*, 2007, **62**, 867–877.
- 106 Z. X. Chen, J. R. Grace and C. J. Lim, *Fuel*, 2008, **87**, 1360–1371.
- 107 P. S. Fennell, R. Pacciani, J. Dennis, J. F. Davidson and A. N. Hayhurst, *Energy & Fuels*, 2007, **21**, 2072–2081.
- 108 L. Jia, R. Hughes, D. Lu, E. Anthony and I. Lau, *Ind. Eng. Chem. Res.*, 2007, **46**, 5199–5209.
- 109 Y. Wu, J. Blamey, E. J. Anthony and F. P. S.
- 110 I. M. Smith, *Properties and behaviour of SO₂ adsorbents for CFBC*, IEA Clean Coal Centre: London technical report, 2007.
- 111 S. Dobner, L. Sterns, R. A. Graff and A. M. Squires, *Ind. Eng. Chem. Process Des. Dev.*, 1977, **16**, 479–486.
- 112 V. Manovic and E. J. Anthony, *Environ. Sci. & Tech.*, 2007, **41**, 1420–1425.
- 113 H. Lu and P. G. Smirniotis, *Ind. Eng. Chem. Res.*, 2009, **48**, 5454–5459.
- 114 V. Manovic and E. J. Anthony, *Environ. Sci. & Tech.*, 2008, **42**, 4170–4174.
- 115 N. H. Florin and A. T. Harris, *Chem. Eng. Sci.*, 2009, **64**, 187–191.
- 116 Z. S. Li, N. S. Cai, Y. Y. Huang and H.-J. Han, *Energy and Fuels*, 2005, **19**, 1447–1452.
- 117 V. Manovic and E. J. Anthony, *Environ. Sci. Tech.*, 2009, **43**, 7117–7122.
- 118 J. S. Dennis and R. Pacciani, *Chem. Eng. Sci.*, 2009, **64**, 2147–2157.
- 119 M. L. Gray, K. J. Champagne, D. Fauth, J. P. Baltrus and H. Pennline, *Int. J. Greenh. Gas Con.*, 2008, **2**, 3–8.
- 120 B. Epple and J. Strohle, 4th International Symposium on In-Situ CO₂ recovery. Imperial College, London, 2008.
- 121 J. C. Abanades, E. J. Anthony, J. Wang and J. E. Oakey, *Environ. Sci. & Tech.*, 2005, **39**, 2861–2866.
- 122 *Cleaner Fossil Fuel Power Generation in the 21st Century*, Uk advanced power generation technology forum (apgtf) technical report, 2009.
- 123 J. C. Abanades, G. Grasa, M. Alonso, N. Rodriguez, E. J. Anthony and L. M. Romeo, *Environ. Sci. Tech.*, 2007, **41**, 5523–5527.
- 124 A. Mackenzie, D. L. Granatstein, E. J. Anthony and J. C. Abanades, *Energy & Fuels*, 2007, **21**, 920–926.
- 125 A. Bosoaga, O. Masek and J. E. Oakey, *Energy Procedia*, 2009, **1**, 133–140.
- 126 *A technology strategy for carbon capture and storage*, Uk advanced power generation technology forum technical report, 2009.
- 127 I. Miracca, K. Aasen, T. Brownscombe, K. Gerdes and M. Simmonds, *Oxyfuel Combustion for CO₂ capture summary*, in *Carbon Capture for Storage in Deep Geologic Formations*, Elsevier, 2005.
- 128 L. Jia, Y. Tan and E. J. Anthony, *Energy and Fuels*, 2009.
- 129 R. Seneviratne, 20th Annual Meeting and Meetings of the Combustion

- and Advanced Power Generation Divisions, 2009.
- 130 D. W. Sturgeon, E. D. Cameron and F. D. Fitzgerald, *Energy Procedia*, 2009, **1**, 471–478.
 - 131 T. Wall, R. Stanger and J. Maier, 1st IEA International Conference on Oxyfuel Combustion, 2009.
 - 132 M. Pinnel and J. E. Bennett, *J. Mat. Sci.*, 1972, **7**, 1016 – 1026.
 - 133 S. Santos, 3rd International Workshop on Oxyfuel Combustion, 2008.
 - 134 R. Sliger, J. Kramlich and N. Marinov, *Fuel Proc. Tech.*, 2000, **65–66**, 423–438.
 - 135 L. Fryda, C. Sobrino, M. Cieplik and W. L. van de Kamp, *Fuel*, 2009.
 - 136 F. Wigley and B. Goh, 1st IEA International Conference on Oxyfuel Combustion, 2009.
 - 137 A. Duncan, B. F. McGhee, C. McGhie, D. W. Sturgeon and F. D. Fitzgerald, 1st IEA International Conference on Oxyfuel Combustion, 2009.
 - 138 L. White, V. M. Torrente, D. Sturgeon and D. Chadwick, *Energy Procedia*, 2009, **1**, 399–406.
 - 139 M. H., M. Radunsky, M. Glausch, T. Witter and D. Hultqvist, 1st IEA International Conference on Oxyfuel Combustion, 2009.
 - 140 G. Beysel, 1st IEA International Conference on Oxyfuel Combustion, 2009.
 - 141 B. R. Dunbobbin and W. R. Brown, *Gas Sep. & Purif.*, 1987, **1**, 23–29.
 - 142 D. Erickson, United States Patent 4132766.
 - 143 Vattenfall website: www.vattenfall.com, 2009, Last checked 16/12/2009.
 - 144 M. Farley, 2008, BCURA Coal Science lecture, available from: www.bcura.org/csl08.pdf.
 - 145 E. Cameron, D. Sturgeon and F. Fitzgerald, International Conference on Coal Science & Technology, 2009.
 - 146 N. G. C. Website, www.newgencoal.com.au.
 - 147 C. Aimard, N., D. Prebende, I. Cieutat, M. Sanchez and R. Tsiava, 1st IEA Conference on Oxyfuel Combustion, 2009.
 - 148 M. Hughes, K., L. Pourkashanian, B. Ma and A. Williams, 1st IEA Conference on Oxyfuel Combustion, 2009.
 - 149 K. Tigges, F. Klauke, C. Bergins, K. Busekrus, J. Niesbach, M. Ehmann, C. Kuhr, F. Hoffmeister, B. Vollmer, T. Buddenberg, S. Wu and A. Kukoski, *Energy Procedia*, 2009, **1**, 549–556.
 - 150 E. Kakaras, A. Koumanakos, A. Doukelis, D. Giannakopoulos and I. Vorrias, *Energy Conv. and Mngt.*, 2007, **48**, 2879–2887.
 - 151 P. Wasserscheid and W. T., *Ionic Liquids in Synthesis*, WILEY-VCH, Weinheim, 2008.
 - 152 J. E. Bara, T. K. Carlisle, C. J. Gabriel, D. Camper, A. Finotello, D. L. Gin and R. D. Noble, *Ind. Eng. Chem. Res.*, 2009, **48**, 2739–2751.
 - 153 J. H. J. Davis, *Chem. Lett.*, 2004, **33**, 1072.
 - 154 J. L. Anthony, S. N. V. K. Aki, E. J. Maginn and J. F. Brennecke, *Int. J. Environ. Technol. Manage.*, 2004, **4**, 105.
 - 155 J. L. Anthony, J. L. Anderson, E. J. Maginn and J. F. Brennecke, *J. Phys. Chem. B*, 2005, **109**, 6366–6374.
 - 156 J. L. Anderson, J. K. Dixon and J. F. Brennecke, *Acc. Chem. Res.*, 2007, **40**, 1208.
 - 157 Y. Hou and R. E. Baltus, *Ind. Eng. Chem. Res.*, 2007, **46**, 8166.
 - 158 P. K. Kilaru, R. A. Condemarin and P. Scovazzo, *Ind. Eng. Chem. Res.*, 2008, **47**, 900.
 - 159 P. K. Kilaru and P. Scovazzo, *Ind. Eng. Chem. Res.*, 2008, **47**, 910–919.
 - 160 P. M. V. C. G. M. F. Jacquemin, J.; Husson, *J. Phys. Chem. B*, 2008, **112**, 2335.
 - 161 D. Morgan, L. Ferguson and P. Scovazzo, *Ind. Eng. Chem. Res.*, 2005, **44**, 4815–4823.
 - 162 A. Finotello, J. E. Bara, D. Camper and R. D. Noble, *Ind. Eng. Chem. Res.*, 2008, **47**, 3453–3459.
 - 163 L. Ferguson and P. Scovazzo, *Ind. Eng. Chem. Res.*, 2007, **46**, 1369–1374.
 - 164 P. A. Hunt, B. Kirchner and T. Welton, *Chem.-A European J.*, 2006, **12**, 6762.
 - 165 M. J. Muldoon, S. N. V. K. Aki, J. L. Anderson, J. K. Dixon and J. F. Brennecke, *J. Phys. Chem. B*, 2007, **111**, 9001.
 - 166 J. E. Bara, C. J. Gabriel, T. K. Carlisle, D. Camper, A. Finotello, D. L. Gin and R. D. Noble, *Chem. Eng. J.*, 2009, **147**, 43.
 - 167 D. Fu, X. Sun, J. Pu and S. Zhao, *J. Chem. Eng. Data*, 2006, **51**, 371.
 - 168 H. Shirota and J. Castner, E. W., *J. Phys. Chem. B*, 2005, **109**, 21576.
 - 169 S. H. Chung, R. Lopato, S. G. Greenbaum, H. Shirota, J. Castner, E. W. and J. F. Wishart, *J. Phys. Chem. B*, 2007, **111**, 4885.
 - 170 F. Mazille, Z. Fei, D. Kuang, D. Zhao, S. M. Zakeeruddin, M. Graetzel and P. J. Dyson, *Inorg. Chem.*, 2006, **45**, 1585.
 - 171 Z. Fei, D. Kuang, D. Zhao, C. Klein, W. H. Ang, S. M. Zakeeruddin, M. Graetzel and P. J. Dyson, *Inorg. Chem.*, 2006, **45**, 10407.
 - 172 T. K. Carlisle, J. E. Bara, C. J. Gabriel, R. D. Noble and D. L. Gin, *Ind. Eng. Chem. Res.*, 2008, **47**, 7005.
 - 173 M. Tamada, T. Hayashi and H. Ohno, *Tetrahedron Lett.*, 2007, **48**, 1553.
 - 174 R. E. Baltus, B. H. Culbertson, S. Dai, H. Luo and D. W. DePaoli, *J. Phys. Chem. B*, 2004, **108**, 721.
 - 175 P. J. Dyson, I. Khalaila, S. Luetzgen, J. S. McIndoe and D. Zhao, *Chem. Commun.*, 2004, **19**, 2204.
 - 176 Y. Chu, H. Deng and J.-P. Cheng, *J. Org. Chem.*, 2007, **72**, 7790.
 - 177 D. Camper, J. E. Bara, D. L. Gin and R. D. Noble, *Ind. Eng. Chem. Res.*, 2008, **47**, 8496.
 - 178 K. Shimojo, N. Kamiya, F. Tani, H. Naganawa, Y. Naruta and M. Goto, *Anal. Chem.*, 2006, **78**, year.
 - 179 J. E. Bara, C. J. Gabriel, S. Lessmann, T. K. Carlisle, A. Finotello, D. L. Gin and R. D. Noble, *Ind. Eng. Chem. Res.*, 2007, **46**, 5380.
 - 180 Q. Liu, M. H. A. Janssen, F. van Rantwijk and R. A. Sheldon, *Green Chem.*, 2005, **7**, 39.
 - 181 S. Hanioka, T. Maruyama, T. Sotani, M. Teramoto, H. Matsuyama, K. Nakashima, M. Hanaki, F. Kubota and M. Goto, *J. Membr. Sci.*, 2008, **314**, 1.
 - 182 C. Myers, H. Pennline, D. Luebke, J. Ilconich, J. K. Dixon, E. J. Maginn and J. F. Brennecke, *J. Membr. Sci.*, 2008, **322**, 28.
 - 183 Z. Fei, D. Zhao, D. Pieraccini, W. H. Ang, T. J. Geldbach, R. Scopelliti, C. Chiappe and P. J. Dyson, *Organometallics*, 2007, **26**, 1588.
 - 184 H. Shirota, J. F. Wishart and J. Castner, E. W., *J. Phys. Chem. B*, 2007, **111**, 4819.
 - 185 K. E. Gutowski and E. J. Maginn, *J. Am. Chem. Soc.*, 2008, **130**, 14690.
 - 186 H. Arakawa, M. Aresta, J. N. Armor, M. A. Barteau, E. J. Beckman, A. T. Bell, J. E. Bercaw, C. Creutz, E. Dinjus, D. A. Dixon, K. Domen, D. L. DuBois, J. Eckert, E. Fujita, D. H. Gibson, W. A. Goddard, D. W. Goodman, J. Keller, G. J. Kubas, H. H. Kung, J. E. Lyons, L. E. Manzer, T. J. Marks, K. Morokuma, K. M. Nicholas, R. Periana, L. Que, J. Rostrup-Nielsen, W. M. H. Sachtler, L. D. Schmidt, A. Sen, G. A. Somorjai and P. C. Stair, *Chem. Rev.*, 2001, **101**, 953–996.
 - 187 M. Aresta, *ACS Symp. Ser.*, 2003, **852**, 2–39.
 - 188 C. A. Eckert, B. L. Knutson and P. G. Debenedetti, *Nature*, 1996, **383**, 313–318.
 - 189 K. S. Lackner, C. H. Wendt, D. P. Butt, E. L. Joyce and D. H. Sharp, *Energy*, 1995, **20**, 1153–1170.
 - 190 *CRC Handbook of chemistry and physics*, ed. D. Lide, CRC Press, Inc., Boca Raton, FL, USA, Seventy fourth edn, 1993–1994.
 - 191 E. E. Benson, C. P. Kubiak, A. J. Sathrum and J. M. Smieja, *Chem. Soc. Rev.*, 2009, **38**, 89–99.
 - 192 J. P. Collin and J. P. Sauvage, *Chem. Rev.*, 1989, **93**, 245–268.
 - 193 D. H. Gibson, *Chem. Rev.*, 1996, **96**, 2063–2095.
 - 194 T. Sakakura, J. C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365–2387.
 - 195 P. G. Jessop, F. Joo and C. C. Tai, *Coord. Chem. Rev.*, 2004, **248**, 2425–2442.
 - 196 M. Aresta and A. Dibenedetto, *Dalton Trans.*, 2007, **28**, 2975–2992.

- 197 <http://www.icis.com/v2/chemicals/9076559/urea/uses.html>.
- 198 D. Kostick, *2009 Minerals Yearbook*, United States Geological Survey, 2009.
- 199 <http://www.sriconsulting.com/PEP/Reports/Phase2003/RW2003-08/RW2003.html>.
- 200 M. Bernard and M.-M. Borel, *Bull.Soc.Chim.Fr.*, 1968, **6**, 2362–2366.
- 201 <http://www.huntsman.com/performance-products/index.cfm?PageID=1596>.
- 202 M. A. Pacheco and C. L. Marshall, *Energy Fuels*, 1997, **11**, 2–29.
- 203 M. Aresta and A. Dibenedetto, *Catal. Today*, 2004, **98**, 455–462.
- 204 T. Sakakura and K. Kohno, *Chem. Commun.*, 2009, **11**, 1312–1330.
- 205 S. P. McGlynn, J. W. Rabalais, J. R. McDonald and V. M. Scherr, *Chem. Rev.*, 1971, **71**, 73–108.
- 206 T. Ohishi, M. Nishiura and Z. Hou, *Angew. Chem. Int. Ed.*, 2008, **47**, 5792–5795.
- 207 K. Ukai, M. Aoki and J. Takaya, *J. Am. Chem. Soc.*, 2006, **128**, 8706–8707.
- 208 T. Tsuda, K. Marata and Y. Kitaike, *J. Am. Chem. Soc.*, 1992, **114**, 1498–1499.
- 209 *Chemical and Engineering News*, 2006, **84**, 59–68.
- 210 <http://www.petrochemistry.net/statistics-western-european-market-review.html#lax>.
- 211 M. Aresta, C. Pastore, P. Giannoccaro, G. Kovacs, A. Dibenedetto and I. Papai, *Chem. -Eur. J.*, 2007, **13**, 9028–9034.
- 212 <http://www.mwponline.co.uk/News/acrylic-acid-from-propane>.
- 213 H. G. Alt, K. H. Schwind and M. D. Rausch, *J. Organomet. Chem.*, 1987, **321**, C9–C12.
- 214 J. C. Bryan and J. M. Mayer, *J. Am. Chem. Soc.*, 1990, **112**, 2298–2308.
- 215 S. H. Hsu, J. C. Chang, C. L. Lai, C. H. Hu, H. M. Lee, G. H. Lee, S. M. Peng and J. H. Huang, *Inorg. Chem.*, 2004, **43**, 6786–6792.
- 216 M. T. Whited and R. H. Grubbs, *J. Am. Chem. Soc.*, 2008, **130**, 5874–5875.
- 217 L. Schmid, M. S. Schneider, D. Engel and A. Baiker, *Catal. Lett.*, 2003, **88**, 105–113.
- 218 S. A. French, A. A. Sokol, S. T. Bromley, C. R. A. Catlow, S. C. Rogers, F. King and P. Sherwood, *Angew. Chem. Int. Ed.*, 2001, **40**, 4437–4440.
- 219 S. N. Riduan, Y. Zhang and J. Y. Ying, *Angew. Chem. Int. Ed.*, 2009, **48**, 3322–3325.
- 220 A. E. Ashley, A. L. Thompson and D. O'Hare, *Angew. Chem. Int. Ed.*, 2009, **48**, 9839–9843.
- 221 P. G. Jessop, T. Ikariya and R. Noyori, *Chem. Rev.*, 1995, **95**, 259–272.
- 222 W. Leitner, E. Dinjus and F. Gassner, *Aqueous-Phase Organometallic Catalysis*, Wiley-VCH, 1998.
- 223 H. Ishida, K. Tanaka and T. Tanaka, *Organometallics*, 1987, **6**, 181–186.
- 224 E. Fujita, *Coord. Chem. Rev.*, 1999, **185–186**, 373–384.
- 225 H. Hori, Y. Takano, K. Koike and Y. Sasaki, *Inorg. Chem. Commun.*, 2003, **6**, 300–303.
- 226 J. Grodkowski and P. Neta, *J. Phys. Chem. A*, 2000, **104**, 4475–4479.
- 227 S. Inoue, H. Koinuma and T. Tsuruta, *J. Polym. Sci., Part B: Polym. Phys.*, 1969, **7**, 287–282.
- 228 G. W. Coates and D. R. Moore, *Angew. Chem. Int. Ed.*, 2004, **43**, 6618–6639.
- 229 D. J. Darensbourg, *Chem. Rev.*, 2007, **107**, 2388–2410.
- 230 O. Ihata, Y. Kayaki and T. Ikariya, *Chem. Commun.*, 2005, **17**, 2268–2270.
- 231 <http://www.us.fjfdi.com/en/cn/project.asp?job=showen&id=9485&yuyan=en>.
- 232 C. M. Byrne, S. D. Allen, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2004, **126**, 11404–11405.
- 233 C. Koning, J. Wildeson, R. Parton, B. Plum, P. Steeman and D. J. Darensbourg, *Polymer*, 2001, **42**, 3995–4004.
- 234 D. R. Moore, M. Cheng, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2003, **125**, 11911–11924.
- 235 D. J. Darensbourg and J. Yarbrough, *J. Am. Chem. Soc.*, 2002, **124**, 6335–6342.
- 236 B. Li, G. P. Wu, W. M. Ren, Y. M. Wang, D. Y. Rao and X. B. Lu, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 6102–6113.
- 237 L. Shi, X. B. Lu, R. Zhang, X. J. Peng, C. Q. Zhang, J. F. Li and X. M. Peng, *Macromolecules*, 2006, **39**, 5679–5685.
- 238 K. L. Peretti, H. Ajiro, C. T. Cohen, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2005, **127**, 11566–11567.
- 239 A. T., I. M. and I. S., *Macromolecules*, 1986, **19**, 8–13.
- 240 D. M. Cui, O. Nishiura, M. Tardif and Z. M. Hou, *Organometallics*, 2008, **27**, 2428–2435.
- 241 Z. Zhang, D. Cui and X. Liu, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 6810–6818.
- 242 K. Nakano, M. Nakamura and K. Nozaki, *Macromolecules*, 2009, **42**, 6972–6980.
- 243 M. R. Kember, P. D. Knight, P. T. R. Reung and C. K. Williams, *Angew. Chem. Int. Ed.*, 2009, **48**, 931–933.
- 244 M. R. Kember, A. J. P. White and C. K. Williams, *Inorg. Chem.*, 2009, **48**, 9535–9542.
- 245 C. C. Pantelides, in *Proc. European Symp. Computer Aided Process Engineering (ESCAPE-11)*, ed. J. S. B. and G. R., Elsevier, Amsterdam, The Netherlands, 2001, ch. New challenges and opportunities for process modelling, pp. 15–26.
- 246 J. C. Charpentier and T. F. McKenna, *Chem. Eng. Sci.*, 2004, **59**, 1617–1640.
- 247 H. M. Kvamsdal, J. P. Jakobsen and K. A. Hoff, *Chem. Eng. Process.*, 2009, **48**, 135–144.
- 248 A. Lawal, M. Wang, P. Stephenson and H. Yeung, *Fuel*, 2009, **88**, 2455–2462.
- 249 J. Strohle, A. Lasheras, A. Galloy and B. Eppe, *Chem. Eng. Tech.*, 2009, **32**, 435–442.
- 250 J. Khinast, G. F. Krammer, C. Brunner and G. Staudinger, *Chem. Eng. Sci.*, 1996, **51**, 623–634.
- 251 R. M. Smith, *Chemical Process Design and Integration*, McGraw Hill, Chichester, 2005.
- 252 J. Oexmann and A. Kather, *Proc. 5th Trondheim Conference on CO₂ capture, transport and storage*, Trondheim, June, 2009, 2009.
- 253 C. P. Galindo, K. Brechtel, S. Hoch, H. Garcia, A. N., H. Hasse and G. Scheffknecht, *Fuel*, 2009, **88**, 2481–2488.
- 254 T. Harkin, A. Hoadley and B. Hooper, *Proc. 12th International Conference on Process Integration, Modelling and Optimisation for Energy Saving and Pollution Reduction*, 2009.
- 255 C. H., M. Lucquiaud, G. J. and L. M., *J. Env. Eng.*, 2009, **135**, 449–458.
- 256 A. Tomasgard, B. A. Pages, O. Klok and S. P. F., *Proc. 5th Trondheim Conference on CO₂ capture, transport and storage*, Trondheim, June, 2009, 2009.
- 257 A. A., *MSc thesis*, Imperial College London, 2008.
- 258 J. Koornneef, T. V. Keulen, A. Faaij and W. Turkenburg, *Int. J. Greenh. Gas Con.*, 2008, **2**, 448–467.
- 259 K. A., N. Z. and D. S., *Int. J. Greenh. Gas Con.*, 2009, **4**, 289–300.
- 260 W. Zhou, B. Zhu, S. Fuss, J. Szolgayova, M. Obersteiner and W. Fei, *Applied Energy*, 2010 Available online 13 February 2010.
- 261 *A technology strategy for carbon capture and storage*, Uk advanced power generation technology forum technical report, 2009.