

# Carbon Capture and Utilisation in the green economy

Using CO<sub>2</sub> to manufacture fuel,  
chemicals and materials



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## Abstract

Carbon capture and storage is seen world-wide as a technology in the global portfolio of mitigation options that can contribute to cost-effective mitigation. However, the past years have shown that significant drawbacks are associated with CCS options that capture CO<sub>2</sub> from an industrial point source or power plant and store it in a geological reservoir. Geological storage is confronted with the possibility of leakage, long-term liability issues, problems with public acceptance of onshore storage locations and limited cost-effective storage capacity in some essential regions. This paper gives a brief technical and economic assessment of a partial alternative to geological storage: carbon capture and utilisation (CCU). For this paper CCU is defined as a process whereby the CO<sub>2</sub> molecule ends up in a new molecule. The paper discusses use of CO<sub>2</sub> for the chemical industry, for mineral carbonation and to grow microalgae. Although these options are for the most part in the R&D phase, they offer potential for value-added applications of carbon dioxide captured from an industrial installation or power plant. In addition, the paper places them in a UK policy context and makes several internationally and UK-relevant recommendations, while exploring their potential contribution to a green economy.

## Acknowledgement

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## Preface/foreword

Ambiguity surrounds the political discussion of capture and utilisation of carbon dioxide (CCU). Confusingly, closely related concepts in the field of CCU have different names; the most common variants are “carbon transformation” and “carbon conversion”. This confusing treatment in the literature and the policy debate combined with a degree of technical and chemical complexity contributes to a lack of support for CCU in the United Kingdom. Through a collaboration between **CO2Chem**, a UK research council project aimed at developing a UK community towards a sustainable chemical feedstock supply by 2050 that is currently running involving numerous universities and industries in the country, and the Energy research Centre of the Netherlands (**ECN**), a well-established Netherlands-based research institution with expertise in the field, this report seeks to clarify the issues around different variants of CCU. The purpose is not to take a position on the merits or drawbacks of carbon utilisation, but to inform decision-makers in government and industry.

In the context of energy and climate policy, governments place much emphasis on carbon capture and geological storage (CCS) as an option that can reduce substantial amounts of greenhouse gas emissions. In order to make CCS a practical reality, however, a considerable cost burden will need to be placed on both the public and private purse. In addition, storage potential may be limited or away from CO<sub>2</sub> sources and public resistance to geological storage of CO<sub>2</sub> has been noted. These are reasons to explore the possibility of substituting part of the demand for geological storage in the conventional CCS-chain with the utilisation of CO<sub>2</sub>, which could add value as well as lower the burden on the directly-needed global geological storage capacity. The debate on carbon utilisation is therefore needed, but has only just begun.

We recycle metals, plastics and paper, so why not carbon? Well, it's not that simple. The technical, economic and social challenges of the different forms of carbon utilisation are diverse, but in the United Kingdom awareness is certainly one of them. This is less of a problem in other countries: the US government has invested over US\$ 1bn on CCU research while the German government has invested €118M in one project with Bayer to research the use of carbon dioxide as a raw material. In the UK, however, to the authors knowledge, no substantial efforts are made to resolve the issues around CCU, and research and technological development activities are minor.

In order to provide the full breadth of possible insights and views, the authors have taken a broad-brush approach to highlight to a non-technical, policymaker audience the most important areas. Many of the issues are subject to scientific debate and even controversy. In order to do them justice, they require further review and understanding. The document

provides a first start for that by remaining evidence-based while providing references for key documents in the field of CCU.

There is no ideal energy and industrial mix, as the recent catastrophe in Japan testifies, and new developments can lead to new insights. This only highlights the complex task ahead for governments. In the full knowledge that views on CCU are divided, the Centre for Low Carbon Futures has commissioned this report, not in order to support the case for or against carbon utilisation, but with the aim of highlighting the technological and commercial potential of CCU that is often not heard. We hope this report is the first in a series of publications on this issue.

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## Executive summary

Capture and storage of CO<sub>2</sub> is defined by most international bodies, including the UK Department of Energy and Climate Change (DECC), as referring to capture of CO<sub>2</sub> from point sources combined with geological storage of CO<sub>2</sub>. While carbon capture and geological storage (CCS) can make a significant contribution to carbon dioxide abatement in the United Kingdom and abroad, there is also the possibility of CO<sub>2</sub> utilisation in building material production, for fuels or in the chemical industry. This paper explains that, in parallel to CCS, capture and utilisation of CO<sub>2</sub> (CCU) can contribute to a green economy and suggests that possibilities for funding technology development be considered.

The United Kingdom has laid down deep greenhouse gas emission reductions in legislation. Next to climate change mitigation, however, economic stability, sustainability of the UK industry to maintain jobs and energy security are important political themes. CCS in some sectors provides cost-effective emission reductions, but has significant shortcomings: it has high investment costs, the potential storage capacity has uncertainties, public resistance to CCS has been increasing, and it costs energy. Moreover, if the UK is to maintain and improve on its current standard of living, access to a secure supply of chemical feedstocks and fuels is essential. Although only a partial solution to the CO<sub>2</sub> problem, under some conditions using CO<sub>2</sub> for CCU rather than storing it underground can add value as well as offsetting some of the CCS costs. The economic potential of CCU is limited by scale, but some options can be attractive enough to pursue.

Mainland Europe, and in particular Germany, the US and Australia are well advanced in research and development of CCU technologies. Substantial investment has been made in those countries by extending CCS technology to incorporate utilisation in addition to storage. New data are emerging daily and so this policy document reflects a snapshot of a point in time. At the time of going to press the Danish government has stated that it will aim to go to a zero-fossil fuel energy economy by 2050. CCU could play a significant role in achieving that aim.

In this policy document, we highlight progress in CCU globally and discuss the opportunities for implementation in the UK in three primary areas: chemical conversion, mineral carbonation and biofuels from algae.

### Chemical conversion to chemical feedstocks and fuels

Rather than treating CO<sub>2</sub> as waste, it can be regarded as a chemical feedstock for the synthesis of other chemicals that do not rely on a petrochemical source. The energy required for this would be best facilitated by renewable



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energy sources, such as wind or solar energy. New catalysts are also necessary. This process can build on current post-combustion CCS technologies to give value-added products that can in theory offset the costs of plant investment or even make the process profitable. Currently, pilot scale technologies only take a slipstream from the main flue gas supply but have the potential and economic viability to be scaled-up. Continuous flow reactor technology and the development of new active and selective catalysts will need to be developed if this CCU option is to play a role at a commercial scale.

## Accelerated mineralisation through carbonisation of rocks

Mineral carbonation involves reaction of minerals (mostly calcium or magnesium silicates) with  $\text{CO}_2$  into inert carbonates. These carbonates can then be used for example as construction materials. Since the energy state of magnesium and calcium carbonates is lower than  $\text{CO}_2$ , theoretically, the process not only requires no energy inputs, but could generate heat. The current bottleneck, however, for a viable mineral carbonation process on an industrial scale is the reaction rate of carbonation. To enhance reaction rates, heat, pressure, chemical processing and mechanical treatment (grinding) of the mineral could be applied, but these treatments are expensive (€60-100/t  $\text{CO}_2$  stored), cost energy and lead to environmental impacts. The potential, globally and in the UK, is considered very large, but the technology is in the R&D phase.



Serpentine: mineral for carbonation

## Biorenewable fuels and materials from algae

Microalgae have a high biomass productivity compared to terrestrial crops and can be cultivated on non-arable land. Many species can grow in salty water. These characteristics could enable sustainable manufacture of products such as bio-oils, chemicals, fertilizers and fuels, replacing fossil fuel-based products. Using flue gases as nutrient supply and  $\text{CO}_2$  source, the cultivation of microalgae in open ponds or photobioreactors could directly capture and utilise  $\text{CO}_2$ . Per tonne of algae biomass ca. 0.5 tonne carbon (from 1.8 tonnes of absorbed  $\text{CO}_2$ ) can be fixed and converted. Microalgae technology is in the R&D phase, and not yet ready for commercial implementation. To achieve cost and energy requirement reductions, leading to viable large-scale algal



Photobioreactors, Solix Biofuels, USA. From: Wiffels & Barbosa, 2010.

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production, significant RD&D investments are needed.

## Recommendations for UK policymakers

As a highly industrialised country, in the UK, all CCU options could be relevant. Given its business-oriented academic community, the UK could play a role and benefit from commercialisation of the technologies involved. If CCU was to be considered in the UK, policy makers should take note of the supply chain of energy and co-reactants to a broad portfolio of products, and develop an appreciation of the market demands for such products. Depending on the process and products, CCU can be profitable with short payback times on investment.

What can UK policymakers do to enable CCU? In the UK, the government could invest in R&D around CCU. Through a strategic policy group, investors could be made aware of potential benefits of CCU and barriers could be brought down. A concrete possibility is whenever CCS is proposed, the possibility of CCU should also be considered. Internationally, recommendations include founding an IEA Implementing agreement on CCU, initiate a Global Technology Roadmap and include CCU in the IPCC Best Practices for greenhouse gas accounting for national greenhouse gas inventories to the UNFCCC.

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## 1 The Rationale for Carbon Capture and Utilisation

Carbon capture and storage (CCS) is most commonly defined as the capture of CO<sub>2</sub> from an industrial or power-sector point source combined with its transport and its storage in geological formations (see e.g. IEA, 2009). CCS is seen as one of the possible technologies in the portfolio of mitigation options that can contribute to cost-effective emission reductions. In theory, CCS facilitates the continued use of fossil fuels while reducing atmospheric CO<sub>2</sub> emissions.

Despite these promises, research and project experience in recent years have shown that considerable drawbacks are associated with CCS options. Capturing CO<sub>2</sub> is associated with high upfront investment costs, highly variable operating costs and in most cases leads to a significant energy penalty. Geological storage is confronted with the challenge of proving that long-term permanent storage is possible as well as resistance of the communities in the vicinity of potential storage locations. Many countries do not have sufficient storage capacity or only have storage potential offshore, for which transport and storage costs are higher. One of those countries is the United Kingdom, but others include Norway, China, most countries in South-East Asia, South Africa, Brazil and India. Life-cycle analyses show that emission reductions are on the order of 65-80% in a coal-fired power plant. Hence, the rate at which CCS projects are deployed and the emission reductions they achieve may be insufficient to effectively contribute to reaching an 80% emission reduction target by 2050.

**Table 1.1** Total UK CO<sub>2</sub> emissions since 1990 (DECC, 2011). The 2009 data does not factor in the likely effects of economic downturn. The 2010 value is provisional.

Year	1990	1995	2000	2005	2006	2007	2008	2009	2010
CO <sub>2</sub> Emissions (Mt)	590	551	549	550	546	538	525	474	492

Table 1.1 shows that while CO<sub>2</sub> emissions are generally reducing year on year, there needs to be a significant step change if the UK 2050 emissions target is to be reached. The 2010 value is provisional but shows how a disruptor can reduce emissions. Unfortunately at this stage this is believed to be economic downturn rather than technological intervention.

Carbon capture and utilisation (CCU) has been suggested as a partial alternative to divert some carbon dioxide from the transport and storage route. While carbon dioxide is considered to be a thermodynamically and chemically stable molecule under standard conditions, it can under certain conditions react with other chemical feedstocks given sufficient energy or using a catalyst to produce value added commodity chemicals (Aresta, 2010; Halmann and Steinberg, 1999) and fuels (Jiang, *et al.*, 2010). Research into CCU is

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relatively well advanced in mainland Europe and the US, but is now lagging behind in the UK despite early efforts. There are good arguments for investing in CCU alongside CCS. First, CCU can be implemented in parallel to CCS, serving additional aims. Second, there are a number of potential benefits that may be harnessed through CCU. Some of the CCU opportunities explored in this report, could benefit the economy by producing value added commodities from waste, and also improve public perception of waste treatment in the UK.

In some countries, research efforts to investigate alternatives to CCS options are already well advanced (BMBF, 2009). Such alternatives explore ways to change the basic characteristics of the CCS supply chain: the use of the CO<sub>2</sub> as a chemical feedstock, as a fertiliser for algae production leading to further CO<sub>2</sub> emission reductions through the sustainable application of those algae, and the mineral conversion of CO<sub>2</sub>. Recently, the Danish Government have proposed a move to zero reliance on fossil fuels by the year 2050 (Denmark, 2011; Mogensen, 2011).

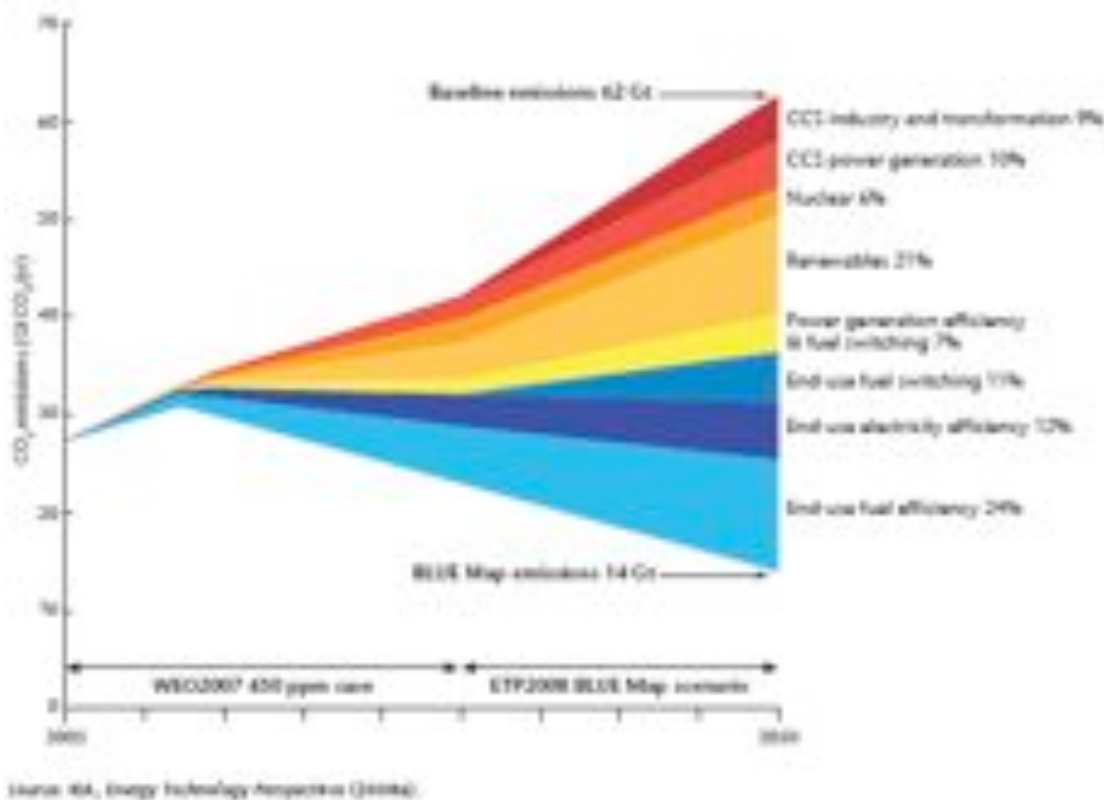
Although such CCU options are still in the research phase, with the current estimated costs therefore high, strategic research can make these options more feasible. It is even possible that costs can be brought down so much that in specific areas, CCU can be more attractive than storing CO<sub>2</sub>. This is demonstrated in the case studies where synthetic liquid fuels and cyclic carbonates are considered as commercial products from CO<sub>2</sub> in flue gas. Although the potential is limited by the market for these products, for countries with high emission reduction ambitions, a strong reliance on imported fuel for its energy needs, limited onshore geological storage opportunities and a research community that is alert to business opportunities, such as the United Kingdom, CCU technologies are worthy of consideration.

This paper gives a brief technical and economic assessment of CCU in the supply chain as an alternative storage option, puts CCU in the UK research and policy context, and explores its potential contribution to a green sustainable economy.

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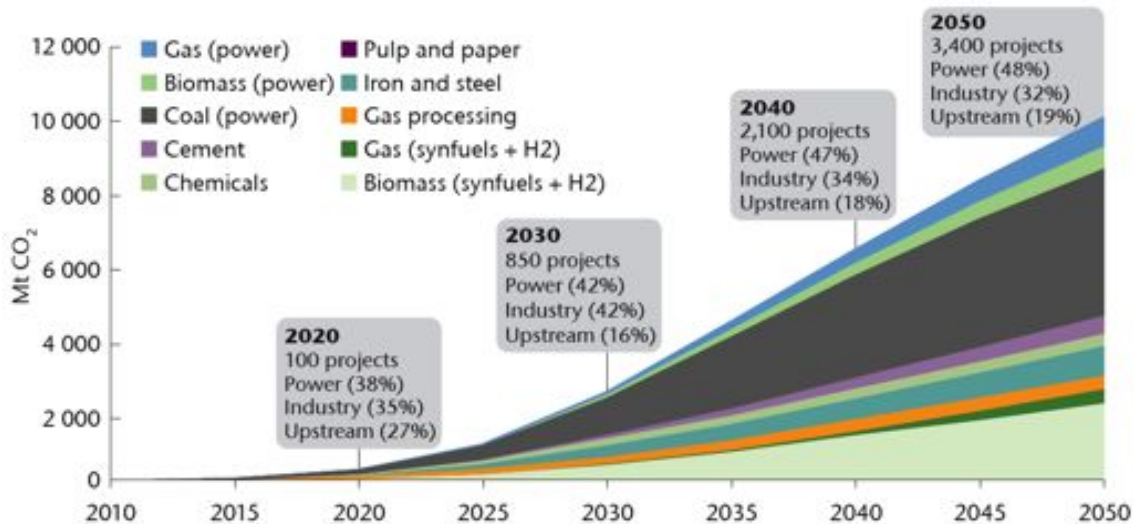
## 2 Introduction to CCS and its policy context

CCS involves the capture of CO<sub>2</sub> from an industrial or power-sector point source combined with its transport, through a pipeline, a dedicated ship or another means, and storage in a geological formation. It is often seen as a significant option in the portfolio of mitigation options (see Figure 2.1) that is important for coal-fired power primarily, but it can also be applied in industrial sectors such as iron and steel and the chemical industry (Figure 2.2). According to the International Energy Agency (IEA), reaching mitigation scenarios consistent with 450 ppm would be 70% more expensive if CCS is omitted from the mitigation portfolio.



**Figure 2.1** Role of CCS in the mitigation portfolio according to the International Energy Agency Energy Technology Perspectives (2008).

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**Figure 2.2** IEA CCS Global Technology Roadmap suggested development of CCS over 2010-2050, by sector (IEA, 2009).

The technical and economic feasibility of CCS is a matter of debate. The IPCC (2005) classified the components of CCS as being in different stages of technological maturity. Some options, such as capture from a limited number of industrial processes, are considered mature as they are implemented routinely, for instance in hydrogen production and gas processing plants. Other components are seen as in or just beyond the demonstration phase – significant-scale demonstrations are operative but the technology is not yet proven at full scale or in commercial conditions in the power sector. Geological storage (in depleted gas- or oil reservoirs, deep unminable coal beds, saline formations or for Enhanced Oil Recovery) has been proven possible in demonstration projects in Norway (Sleipner project) and Algeria (In Salah), and the US has been commercially operating Enhanced Oil Recovery programs for over 40 years. However, the development of universally agreeable predictive models and comprehensive monitoring techniques must still be established.

Assessing the market readiness of capture technologies is complicated, as many of the techniques put forward from equipment manufacturers have yet to be proven by application in a full-scale power plant. Geological storage reservoirs are all unique and require significant exploration before it can be concluded that they are suitable for CO<sub>2</sub> storage, and provide concrete indications on the total storage capacity. The past years have seen several cases of CCS projects being cancelled for technical reasons, although when CCS experts are asked for the main barriers, technological barriers are usually not high on their list. Geological storage capacity is difficult to estimate (IPCC, 2005; Meer and Egberts, 2008). Therefore, although the estimates cited in literature and used for modelling usually indicate sufficient storage capacity (IPCC, 2005; IEA, 2008), there remains a certain level of uncertainty. Currently, five full-scale CCS operations are ongoing: two offshore gas processing projects with storage in a saline formation in Norway (Sleipner, Snøhvit), two

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CO<sub>2</sub>-EOR projects, one in Canada (Weyburn) and one in the US (Rangely), and a gas processing and storage in a gas reservoir project in Algeria (In Salah). Except for a small leakage in the In Salah project due to a malfunctioning wellhead, none of these projects have shown proven leakage from the reservoir.

Costs of CCS are considered to be highest for the capture component, but storage and especially transport costs can also be significant. Current capture costs are believed to be in the region of 75-90 USD/tCO<sub>2</sub> (Mckinsey and Company, 2008); they may come down as a result of innovation and economies of scale. Storage costs depend on the monitoring techniques suitable for the reservoir, the presence of existing infrastructure and the injectivity (the ease of CO<sub>2</sub> injection). Transport cost can escalate with long distances, low volumes and difficult terrain. At the same time, capture cost can be low, when the source of CO<sub>2</sub> is from a process that results in high-purity CO<sub>2</sub>. A major issue affecting costs of capture is the energy requirement of the capture process, which currently has a considerable negative effect on the efficiency of a power plant or the economics of an industrial facility. Some processes for reducing this energy penalty that are currently researched are showing promise of lower energy penalties, but it is unclear at the moment whether these processes, such as chemical looping, can be commercialised. In addition to the costs, barriers to CCS include public perception, which has also led to the cancellation of at least three CCS projects worldwide. Legislation on CCS is implemented in some countries, including the European Union, but still pending in many others (IEA, 2011).

The European Union is the only jurisdiction with a structural incentive for CCS: The EU Emissions Trading Scheme, with a carbon price of currently 11-15 €/tCO<sub>2</sub>. This is, however, not a sufficient incentive for CCS given the costs and perceived investment risk due to the first-of-a-kind character of the technology. Governments in the EU, Canada, Australia and the United States have committed large sums of financial support to demonstrate CCS in various sectors. Globally, this funding amounts to the equivalent of US\$ 20 billion. Some developing countries are also investing in CCS, in particular China, Brazil and several countries in the Middle East. Enhanced Oil Recovery is a driver in many of these cases. In terms of incentives beyond EOR in developing countries, CCS is, after a long and controversial debate, currently eligible in the Kyoto Protocol's Clean Development Mechanism, however a list of procedural barriers still need to be overcome.

Current state of the art post-combustion CCS uses a variety of capture agents; however these are mainly based on ethanolamines such as MEA. There have been a number of recent concerns over the use of these capture agents, related to their corrosivity, volatility under operational conditions and the release of hazardous capture agents into the atmosphere (Aaron & Tsouris, 2005), particularly recently in Norway. Furthermore, there are considerable capital expenditure costs associated with the use of amine capture agents. These are used not in their pure form but as solutions in water, which acts as a solvent. Maximum amine concentrations of 30% are typically used which means that 70% of the

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adsorber and desorber unit contain water which, while contributing to the overall efficiency of the process (Puxty, *et al.*, 2009; Idem, *et al.*, 2006; Yeh, *et al.*, 2005), is present in huge excess. Additionally, because the adsorber-desorber units typically operate in the temperature range 50-120°C water vapour combined with the amine in the vapour phase can significantly increase the corrosion in process pipe and so increases construction and maintenance costs. There is therefore considerable effort required to produce new capture agents with better environmental credentials. Recent studies have shown that solid capture agents such as functionalised silicas (Song, 2006), poly(ionic liquid)s (Supasitmongkol & Styring, 2010), activated carbons (Wahby, *et al.*, 2010) and calcium oxide (Blamey, *et al.*, 2010) can be used to not only enhance capture but also reduce the capital expenditure required on plant construction. While the ideal solution would be to build new low carbon powerplants, the current situation in the UK required post combustion retrofitting of existing plants in the short to medium term whilst new precombustion plants are being designed.

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## 3 Introduction to CCU technologies

Carbon Capture and Utilisation (CCU) can be regarded as addressing two related issues. While CCS alone is a technology directed to CO<sub>2</sub> abatement it removes carbon from the economy. CCU alone takes CO<sub>2</sub> from point sources then converts it into commercially valuable products. However, CCU alone cannot realistically remediate all emissions because of the volumes involved and the potential markets for the individual products. Furthermore, due to the energy penalty with CCU, it is likely that the conversion steps will take place at times of low energy demand, when renewable electricity is comparatively cheaper.

Other factors that govern the commercial viability of CCU also need to be considered. These include the availability of hydrogen and other feedstocks in the supply chain and a systems approach to integration of resources, energy and land use.

### 3.1 Chemical feedstocks

Carbon dioxide (CO<sub>2</sub>) is a non-polar, chemically unreactive molecule under standard conditions that therefore persists in the atmosphere. It occurs naturally through the combustion of carbonaceous materials and volcanic activity, but is also a major pollutant from anthropogenic utilisation of carbonaceous materials. As a consequence of its low reactivity, if CO<sub>2</sub> is to be converted into economically valuable products there has to be an energy trade off or a reduction in the activation energy for the reaction through the use of catalysts. Because of the enormous quantities of CO<sub>2</sub> emitted through anthropogenic activities, it is necessary for these processes to be diverse because of supply chain requirements and global capacity.

A driver for investment in carbon dioxide utilisation will be the ability to maintain security in the supply of fuels and commodity chemicals that have traditionally relied on petrochemical feedstocks. Petrochemical prices are indexed to crude oil prices and fluctuation can lead to supply and price instabilities. By utilising CO<sub>2</sub> it is possible to retain carbon within a cycle. It may be that the carbon is trapped in a permanent form, such as through accelerated mineralisation, to produce construction materials and polymer formation, or stored within an energy vector, such as a synthetic liquid fuel. However, with conversion to fuels, capture of CO<sub>2</sub> from the air would ultimately be necessary to maintain the cycle. Within the wide spectrum of possible products there are valuable intermediates including synthesis gas and small molecule organics that can be targeted.

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The following figure shows some of the important transformations of CO<sub>2</sub> that have been reported to date. This represents a small sub-set of the whole chemicals landscape and it is only recently that efforts have been focused on diversifying the portfolio of reactions. This is an area that has been identified by the Engineering and Physical Sciences Research Council (EPSRC) in their Grand Challenges looking towards a sustainable chemical economy by 2050. Therefore, research into how CO<sub>2</sub> can be effectively utilised is an area of great interest and prime for investment. Indeed, the International Conference on Carbon Dioxide and Utilisation<sup>1</sup> is growing year on year and new reaction pathways are being discovered at an increasing rate.

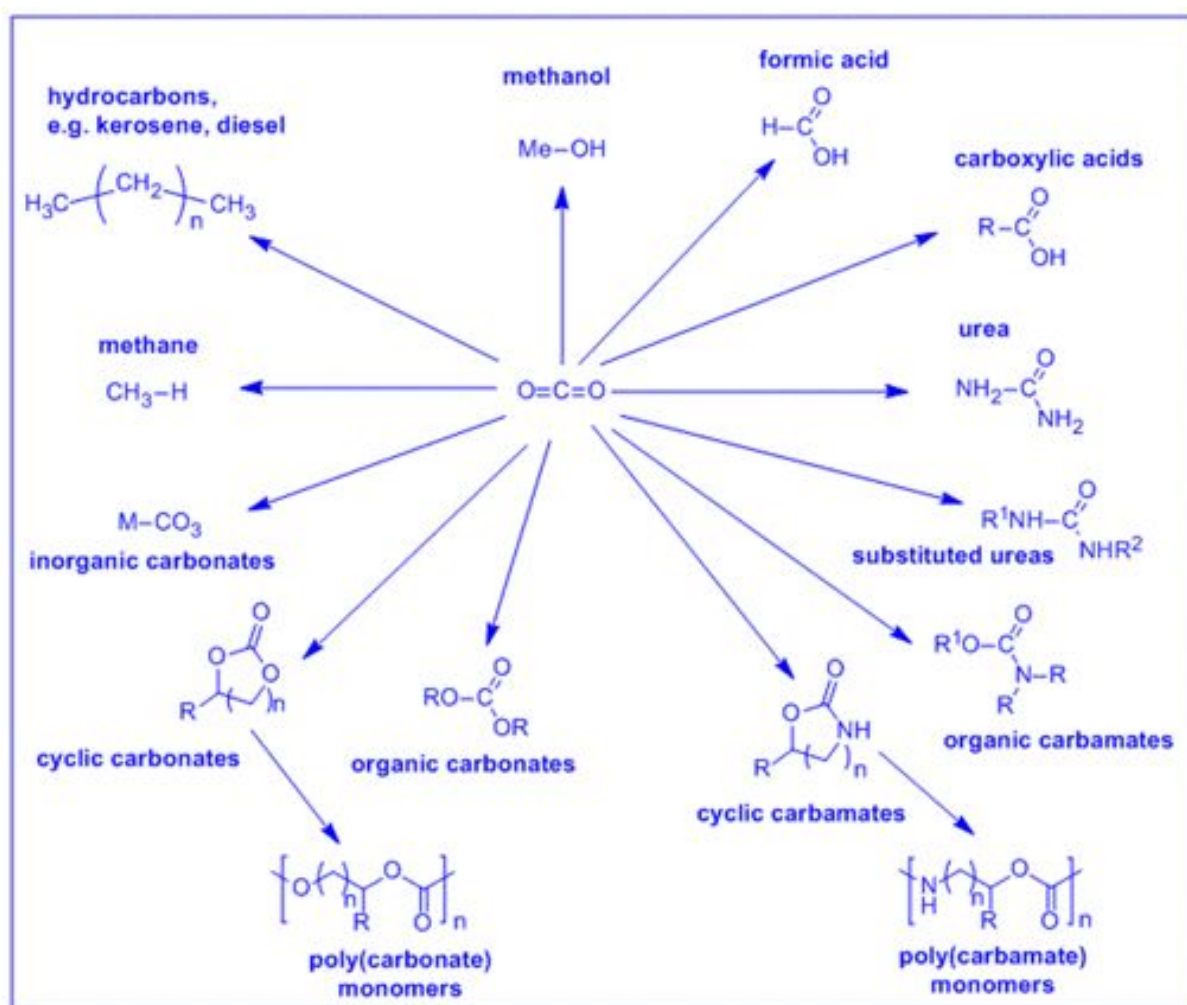


Figure 3.1 A brief overview of chemicals from carbon dioxide.

<sup>1</sup> <http://www.fcc-asso.fr/iccd/>

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## 3.2 Mineral carbonation

The concept of storage of CO<sub>2</sub> as calcium and magnesium carbonate minerals is commonly referred to as mineral carbonation (IPCC, 2005). Calcium and magnesium carbonates are poorly soluble in water and are environmentally harmless minerals that could provide a permanent storage solution for CO<sub>2</sub>. Mineral carbonation could be an alternative for long-term geological storage, especially for regions where CO<sub>2</sub> underground storage is not possible.

In mineral carbonation, (captured) CO<sub>2</sub> is reacted with minerals (mostly calcium or magnesium silicates) to form (Ca or Mg) carbonates. As mineral feedstock, rocks that are rich in alkaline earth silicates can be used. Examples are olivine (MgSiO<sub>4</sub>) and wollastonite (CaSiO<sub>3</sub>). These silicates of magnesium and calcium react with CO<sub>2</sub> to form the corresponding carbonates and SiO<sub>2</sub> providing storage on a geological time scale. Carbon dioxide storage by mineral carbonation mimics the naturally occurring rock weathering which is known to have played an important role in the historical reduction of the CO<sub>2</sub> concentration in the atmosphere after the creation of the earth. This “weathering” depends on the initial chemical composition, the characteristics of the minerals and the amount of CO<sub>2</sub> uptake.

The natural carbonation reaction is very slow. Therefore, a key challenge for large-scale industrial deployment of CO<sub>2</sub> mineralisation is acceleration of the carbonation process, using heat, pressure, and mechanical and chemical pre-treatment of the mineral. The carbonation reactions are all exothermic indicating that in principle no net energy is required for the reactions to take place and that theoretically even useful energy *i.e.* heat could be produced, but the energy from the reaction needs to be recovered. The technology of accelerated carbonation has been used in the treatment of solid wastes in which toxic compounds are stabilised by carbonated materials, so that the treated solid waste material can be utilised in construction.

The key advantages of mineral carbonation for CO<sub>2</sub> storage are:

1. It is the only form of CO<sub>2</sub> storage that is a permanent, leak-free fixation with no need for long term monitoring.
2. A potentially very large capacity. The calcium and magnesium carbonate mineral rock deposits on earth are theoretically sufficient to fix all the CO<sub>2</sub> that could be produced by the combustion of all available fossil fuel reserves (Lackner *et al.*, 1995).
3. The carbonation chemical reactions are all exothermic indicating that in principle no energy is required for the reactions to take place and that theoretically even useful energy *i.e.* heat could be produced.
4. Waste materials like steel converter slag or asbestos can be converted into “valuable” calcium or magnesium carbonates.
5. Finally, it is technically possible to operate the carbonation process directly with flue gases, making the expensive CO<sub>2</sub> capture step superfluous.

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Disadvantages associated with the process are:

1. Large volumes of minerals are required and need to be transported from the mining place to the carbonation plant. Transport distance can be minimized by situating the carbonation plant at the site of the mine.
2. To fix a tonne of CO<sub>2</sub> requires about 1.6 to 3.7 tonnes of rock, so that more than six times more rock than coal is required to be mined to fix the CO<sub>2</sub> from its combustion.
3. Although in principle no energy is required for the carbonation process, storage efficiency will be less than 70% due to energy consumption related to mining, transport and pre-processing of the minerals, requiring grinding to around 100 microns.
4. Extensive mining operations necessary, which will have environmental impact.
5. There is the potential for asbestos to be present in the mineral deposit.

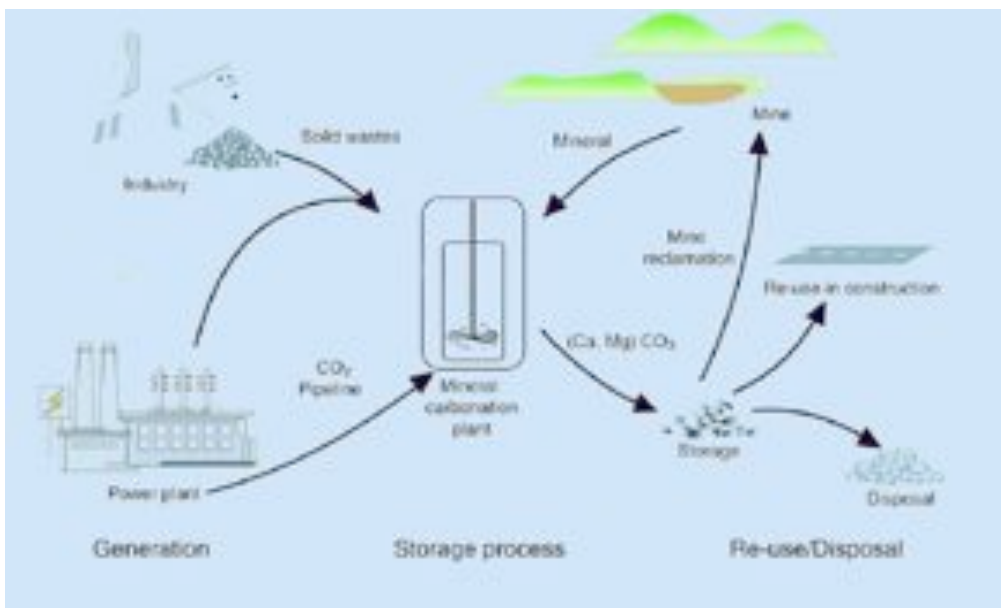


Figure 3.2 Summary of mineral carbonation options (Huijgen, 2007; IPCC, 2005).

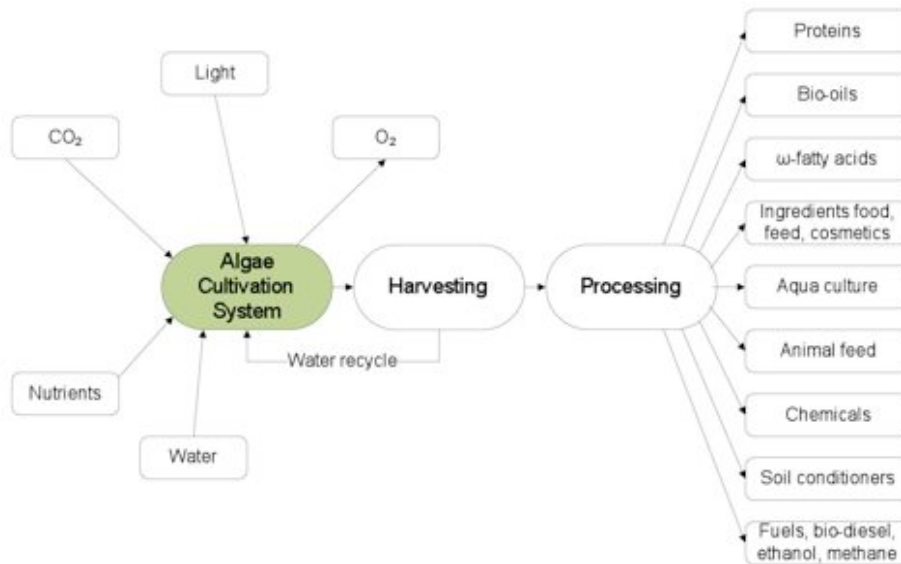
## 3.3 Value-added CO<sub>2</sub> utilisation through algae

Biological mitigation of CO<sub>2</sub> relies on photosynthesis by green plants or algae. In this process organic compounds are synthesised from carbon dioxide and water powered by energy derived from sunlight. The resulting biomass can be used for electricity generation or as raw material for production of transportation fuels, bio-based chemicals and materials. An option for direct capture and utilisation of CO<sub>2</sub> emitted from point sources could involve the cultivation and processing of plants growing in an aquatic environment especially microalgae.

Microalgae are microscopic, single-celled plants growing in fresh water or seawater. They use sunlight as their energy source, and CO<sub>2</sub> and inorganic nutrients (mainly N-compounds (NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>) and phosphates) for growth. The CO<sub>2</sub> for algal growth can be derived from concentrated sources such as flue gas. Per tonne of algal biomass ca. 0.5 tonne carbon

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(from 1.8 tonnes of CO<sub>2</sub> taken up by the algae) are fixed and converted to valuable products. Micro-algal biomass is a versatile raw material that can potentially be used as a source for a range of non-fuel and fuel products, including bio-oils and proteins, high value chemicals and ingredients, food and feed, fertilizers and fuels.



**Figure 3.3**  
Overview of Algae production process and product options.

In recent years large investments have taken place in the sector by private investors and governments in the US, the EU and elsewhere predominantly aimed at fuel production. However, to date no successful large-scale production of algal biofuels has been realised.

An important feature is the high growth rate and productivity of micro-algae, which is several fold higher than most terrestrial plants. This is due to more efficient use of light and highly efficient utilisation of nutrients by the microalgae. Cultivation takes place in open-pond systems or in (semi)closed photobioreactors that could be located on marginal, non-arable land. Many algal species can use salt or brackish water or effluents so in these applications there is no competition with conventional agriculture. Due to evaporation some form of salt management must be used such as brine removal. A disadvantage is the relatively high energy requirement for continuous mixing of the cultivation system and for dewatering of the algal biomass.

Even though CO<sub>2</sub> utilisation through algae has advantages and potential, there are several major challenges. Even at higher productivities microalgal systems have a substantial land requirement, which may not be available in the direct surroundings of power plants. Furthermore, costs are still high. Significant R&D and technological development and cost reductions related to cultivation and harvesting of the algae are required to enable large-scale production systems.

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## 3.4 International context

The UK at present lags behind most developed countries in terms of investment and focus on CCU. Currently the majority of UK funding is being spent on CCS, however many other countries, including the USA, are placing a greater emphasis on CCU. Since 2008 the Engineering and Physical Sciences Research Council (EPSRC), the main source of UK government research funding to universities in this area, funded eight projects to a total of £4.9 million on CCU and fifteen projects (total £11.8 million) on CCS. The UK government is investing £1 billion in the first CCS demonstration project, but currently there are no plans for investment in demonstration scale CCU technologies unlike Germany, USA and Australia.

In a speech to the United States Senate, Margie Tatro, director of Fuel and Water Systems at Sandia National Laboratories, advocated that carbon recycling is the way of the future; “We must act now to stimulate this area of research and development,” Tatro said. “Other countries are exploring reuse and recycling of CO<sub>2</sub>, and it would be unfortunate if the U.S. became dependent on imported technology in this critical area”<sup>2</sup>. To this end the US has invested over \$100 million in CCU research in the following areas: CO<sub>2</sub> mineralisation, scrubbers that transform gases into carbonate/bicarbonate products, CO<sub>2</sub> based plastic manufacturing and new fuel technologies based on algae and CO<sub>2</sub>.<sup>3</sup> A number of these processes are in the large-scale pilot testing phases, with commercialisation occurring in the next few years.

Starting in 2009, the German government has set aside €118 million over five years to fund research into the use of carbon dioxide as a raw material. The research programme is expected to develop new processes using CO<sub>2</sub> as a base chemical, for example for the development of high-value polymers. This funding has allowed Bayer to open a pilot plant to trial on a technical scale a process to directly manufacture polyurethanes using CO<sub>2</sub> in February 2011<sup>4,5,6</sup>.

In China, the Huaneng Group who are the country’s largest power generation company have two pilot scale projects for CCS. A proportion of the CO<sub>2</sub> is captured and then sold for reuse in the food industry and for other industrial applications. This is seen as an important factor in the commercial viability of the plants as selling the CO<sub>2</sub> offsets the costs of capturing the gas<sup>7</sup> and negates the need to manufacture or buy CO<sub>2</sub>.

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<sup>2</sup> [http://www.fossil.energy.gov/recovery/projects/beneficial\\_reuse.html](http://www.fossil.energy.gov/recovery/projects/beneficial_reuse.html) Last accessed 21.03.2011

<sup>3</sup> <http://www.mantraenergy.com/Portals/MantraEnergy/pdf/articles/carbon%20recycling%20article%20by%20Rowan%20Oloman.pdf> Last accessed 22.03.2011

<sup>4</sup> <http://www.bmbf.de/press/2634.php> Last accessed 23.03.2011

<sup>5</sup> [http://www.dnv.com/binaries/DNV-position\\_paper\\_CO2\\_Utilisation\\_tcm4-445820.pdf](http://www.dnv.com/binaries/DNV-position_paper_CO2_Utilisation_tcm4-445820.pdf) Last accessed 23.03.2011

<sup>6</sup> <http://www.research-in-germany.de/60972/2011-02-21-bayer-stars-pilot-plant-for-plastic-manufacturing-with-co2.html> Last accessed 22.03.2011

<sup>7</sup> <http://www.npr.org/templates/story/story.php?storyId=102920210> Last accessed 23.03.2011 and

<http://www.globalccsinstitute.com/community/blogs/authors/kristinastefanova/2011/02/25/what-china-doing-ccs>

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Methanol for renewable fuel for cars produced from CO<sub>2</sub> emissions and geothermal power, is currently being researched and manufactured in Iceland. Carbon Recycling International Ltd is currently building a plant (due for completion March 2011 to produce 5 million litres of renewable methanol per annum, which will be blended with gasoline or diesel before it enters the fuel market <sup>8</sup>.

Australia hosts the Global CCS Institute and is at the forefront of CCS research. The institute along with studying CCS is researching CO<sub>2</sub> re-use. The Australian government has invested AU\$40 million in the Calera mineralisation project, which aims to use CO<sub>2</sub> captured from the Yallourn power station to make cement and aggregate material <sup>9,10</sup>.

In Norway, risk management experts Det Norske Veritas (DNV) have concluded in a 2011 position paper<sup>11</sup>, that in order to maintain the supply chain in chemical feedstocks it is essential to use CO<sub>2</sub> as a precursor and alternative to petrochemical feeds.

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<sup>8</sup> <http://www.carbonrecycling.is/index.html> Last accessed 23.03.2011 and <http://www.carbonrecycling.is/Announcements/Carbon%20Recycling%20Press%20Release%20December%206%202010.pdf> Last accessed 23.03.2011

<sup>9</sup> <http://minister.ret.gov.au/MediaCentre/MediaReleases/Pages/FundingforAustralia%27sFirstCarbonCaptureandUseProject.aspx> Last accessed 23.03.2011

<sup>10</sup> <http://www.pm.gov.au/press-office/new-funding-institute-support-carbon-capturing> Last accessed 23.03.2011

<sup>11</sup> [http://www.dnv.com/binaries/DNV-position\\_paper\\_CO2\\_Utilisation\\_tcm4-445820.pdf](http://www.dnv.com/binaries/DNV-position_paper_CO2_Utilisation_tcm4-445820.pdf) Last accessed 23.03.2011

## 4 Conversion of CO<sub>2</sub>: chemical feedstock

- Rather than treating CO<sub>2</sub> as waste, it can be regarded as a precursor for the synthesis of chemical feedstocks that do not rely on a petrochemical source.
- By integrating renewable energy sources, such as wind or solar energy, and catalysts into the process it is possible to produce valuable chemical intermediate and products.
- This raises the possibility of building on existing post-combustion CCS technologies to give value added products that can in theory offset the costs of plant investment or even make the process profitable.
- This section will review existing chemical processes for CO<sub>2</sub> utilisation and highlight areas where advances may be made to embrace carbon capture and utilisation (CCU) within the UK in order to maintain a stable and secure supply of chemical feedstocks.

### 4.1 Introduction

While CO<sub>2</sub> has low chemical activity, it is possible to activate it towards reaction through the use of catalysts, temperature and pressure. As carbon in CO<sub>2</sub> is in the oxidised form, many of the resulting reactions are reductions, either through the addition of hydrogen or electrons. The exceptions are CO<sub>2</sub> insertion reactions where there is no overall change in oxidation state. While catalysts can play a significant role in reducing the activation energy and the total energy required for a reaction, it is likely that there will also need to be a considerable energy input to make it viable. The energy cost must therefore be factored in when considering the economic viability of a process and product, and it is realised that this energy must come from renewable sources. Furthermore, the supply of co-reactants must also be taken into account, particularly given the huge quantity of CO<sub>2</sub> that is currently emitted, in order that supply chain security is maintained. Chemicals from CO<sub>2</sub> can be subdivided into a number of important areas.

CO<sub>2</sub> is already used in commercial processes, both in its pure form and as a feedstock in the synthesis of bulk chemicals such as urea. In the pure form CO<sub>2</sub> is presently used in the food industry with uses as varied as carbonation of drinks to accelerated production of greenhouse tomatoes. Likewise, large quantities are also used as solvents in processes such as dry fabric cleaning and decaffeination. The CO<sub>2</sub> is eventually released back to the atmosphere so these are recycling rather than mitigation technologies. The versatility of supercritical CO<sub>2</sub> (scCO<sub>2</sub>) is that it can be used to solubilise many organic molecules and can be removed at the end of a process by evaporation to leave pure organics without solvent residue as a contaminant. As a food additive or solvent CO<sub>2</sub> is again only stored

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transiently and is re-released after use. CO<sub>2</sub> has also been used in enhanced oil and gas recovery by pumping it under near critical or supercritical conditions into oil fields where conventional recovery has become uneconomical or impractical.

While CCU appears to be an ideal solution, especially when coupled with CCS, there are of course barriers to implementation. An obvious barrier is the unfavourable thermodynamics of many conversions that means that there will be an energy cost associated with utilisation. A second issue is supply capacity, both in terms of co-reactants in any process and also in market demand for the product. It has been suggested in a position paper from VCI and DECHEMA in Germany (2009) that chemical industries could convert at most around 1% of global CO<sub>2</sub> emissions in the fine and bulk chemicals sector and 10% into synthetic fuels. However, Aresta (2010) is more optimistic and estimates chemical synthesis could account for 7% of the CO<sub>2</sub> emissions. Therefore, CCU should not be regarded as an alternative technology to CCS but as a complementary technology. The low values predicted for utilisation are related to market demand for current products and the capital expenditure required for plant construction. The former should be addressed by identifying new C-1 chemistries and catalytic processes, while the latter can be reduced by process intensification, including the development of new capture agents with higher efficiencies and smaller volumes.

### 4.2 Fuels

CO<sub>2</sub> is a direct product from fuel combustion so needs to be converted to a higher energy form if it is to be re-used as a synthetic liquid fuel. Therefore, synthetic fuel products from CO<sub>2</sub> should be regarded as energy vectors or energy stores, utilising renewable energy sources at off-peak times with temporarily stored local CO<sub>2</sub>. The amount of energy required to produce liquid synthetic fuels exceeds the recoverable energy, however it is a way of storing excess energy in a more useable form. The general class of reactions are known as reforming reactions and include hydrocarbon and carbon reforming reactions and hydrogen reforming (hydrogenation) reactions (Jiang, *et al.*, 2010; Song, 2006; Halmann & Steinberg, 1999).

Methanol and formic acid have been widely targeted as products. Both are formed by hydrogenation of CO<sub>2</sub> over a wide range of catalysts. Methanol synthesis requires three equivalents of hydrogen per molecule of CO<sub>2</sub>, two being incorporated into the product with the third being consumed in the production of the by-product, water. Formic acid is a valuable product in that it can store hydrogen in a more manageable liquid form, requiring only a single equivalent of hydrogen and without the formation of by-products and so is highly atom efficient. Subsequent decomposition of formic acid releases the hydrogen when required but also re-releases the CO<sub>2</sub>.

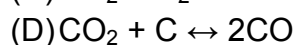
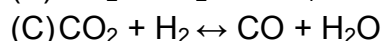
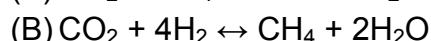
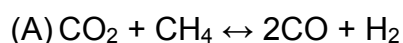
# Carbon Capture and Utilisation in the green economy

Synthetic liquid hydrocarbon fuels have become increasingly targeted for CCU in recent years (Jiang, *et al.*, 2010; RSC, 2006). Such fuels may be necessary to maintain a secure supply of transportation fuels without reliance on supply from politically unstable countries, particularly in the case of aviation and long-haul sea and road transport where electric batteries cannot provide the necessary range between re-charging. Again there is an energy issue, but there are additional problems in that considerable quantities of hydrogen are required, and selectivity to produce a single fraction of commercially valuable fuels such as kerosene or diesel still remains poor. However, it should be noted on the positive side that the production of synthetic fuels reduces exploration costs and produces a refined rather than a crude product. Sandia Laboratories in New Mexico, USA have reported the synthesis of synthetic diesel from CO<sub>2</sub>, the required energy being achieved using a solar furnace. Air Fuel Synthesis in the UK have used atmospheric CO<sub>2</sub> and wind energy to produce A1 aviation fuels on a pilot plant facility at an initial rate of 1 litre per day which will be five times up-scaled on a demonstrator unit (see Case Study 1).

Pearson *et al.* (2009) state “The fundamentals of physics and electrochemistry dictate that the energy density of batteries and molecular hydrogen is unlikely ever to be competitive with liquid fuels for transport applications”. For this reason it is necessary to consider the conversion of renewable energy into a usable liquid form, which can be used in conventional combustion engines without major, costly modification.

## 4.3 Intermediates

While direct products are a key target in CCU, intermediates represent a huge potential market. The chemicals industry currently relies on intermediates derived from petrochemical sources, with a small proportion coming from natural products. An important intermediate is synthesis gas (carbon monoxide and hydrogen, also known as syngas) which can be separated or used directly in the synthesis of hydrocarbon fuels. The importance of intermediate formation will become increasingly clear as fossil fuels become further depleted. The production of intermediates from CO<sub>2</sub> will build on existing chemistries but it is also recognised that new, efficient C11 chemistries will need to be developed. Synthesis gas is produced by a variety of reforming reactions, sometimes in multiple steps, including methane reformation (A), the Sabatier process (B), the reverse water-gas shift reaction (C) and carbon gasification (D):



One of the benefits of reforming reactions is the simplicity of the catalysts used, including nickel and cobalt catalysts. The synthesis gas produced can then be used in the transition

## Carbon Capture and Utilisation in the green economy

metal catalysed Fischer-Tropsch (F-T) synthesis. Alternatively, CO<sub>2</sub>-H<sub>2</sub> mixtures can also be used but the complexity of the catalysts increases to the point that they do not become chemically viable on a scaled-up reactor. There is therefore a challenge to develop not only the F-T process conditions but also to design new effective and selective catalysts.

### 4.3.1 Urea

Large quantities of CO<sub>2</sub> are already consumed through reaction with ammonia from the Haber-Bosch process to produce urea (H<sub>2</sub>N-(C=O)-NH<sub>2</sub>), a key ingredient in fertilisers. This is an established and commercially viable technology that already produces the annual global supplies of urea, and is therefore a saturated market. However, this cannot be regarded as a carbon negative process using a whole systems approach as there is a large energy requirement in the synthetic process and fertiliser is regarded as one of the major sources of agricultural emissions. There is considerable scope for the production of diverse derivatives which themselves are useful feedstocks in the pharmaceuticals, fine chemicals and polymer industries.

### 4.3.2 Carbamates

The reaction of a variety of N-nucleophiles with carbon dioxide results in the formation of N-carbonyl compounds, including carbamates. These are useful synthetic building blocks and have applications ranging from pesticides for agricultural processes to polymers for construction and protection. Quaranta and Aresta (2010) have published an excellent review of N-carbonyl compounds from CO<sub>2</sub> which also includes the urea derivatives discussed above. Carbamates differ from ureas in that the central carbon of the C=O group is also bonded to a nitrogen and an oxygen, rather than the two nitrogens in urea. One of the most useful uses of carbamate esters is as a replacement for the extremely toxic reagent phosgene in organic synthesis (Adams & Baron, 1965; Hagemann, 1985; Rossi, 2005). Carbamates are also useful precursors in the synthesis of isocyanates which are used in the formation of poly(urethane)s.

### 4.3.3 Carboxylation

The direct addition of CO<sub>2</sub> to a suitable receptor molecule is atom efficient in that all atoms are incorporated in the product. The bond formed is a single bond to the carbon atom on CO<sub>2</sub> to form a carboxylate group, most commonly as a carboxylic acid. There are many examples of processes producing carboxylic acids from CO<sub>2</sub> including the Kolb -Schmidt reaction to produce salicylic acid from phenol. A step further is the formation of organic carbonates from CO<sub>2</sub>. Linear organic carbonates are formed from alcohols and are useful as solvents so have a substantial potential market. Cyclic carbonates require a little more thought in terms of the supply chain for the co-reactants but these can be naturally sourced. CO<sub>2</sub> undergoes an insertion reaction into an organic epoxide to give the cyclic carbonate (see Case Study 2), which can then be used as a solvent and also an intermediate in organic and polymer synthesis.

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## 4.3.4 Cycloaddition or CO<sub>2</sub> Insertion Reactions

This is another atom efficient process however two bonds are formed, one to the carbon and a second to one of the oxygens. The process requires a second molecule with two conjugated double bonds to proceed. At present there are a few reports detailing this chemistry (Halmann & Steinberg, 1999) but it also represents an area for future exploitation, particularly as useful pharmaceutical molecules can be synthesised.

## 4.3.5 Inorganic Complexes

In addition to accelerated mineralisation, the production of inorganic carbonates is widespread using a diversity of metal cations as the molecular template. The resulting complexes have numerous applications in construction as well as catalysis, and given the wide geological availability of starting materials represent a significant area for future commercial exploitation.

## 4.3.6 Polymers

Cyclic carbonates with more than six atoms can be ring-opened to give a hydroxy carboxylic acid that can be polymerised to give a poly(carbonate). However, there is now considerable effort in the direct synthesis of the polymers from CO<sub>2</sub> and an epoxide. Poly(carbonate)s are used extensively in construction materials in place of glass and in security and personal protection products due to its high strength and impact resistance while being extremely light and mouldable. The chemical and mechanical properties of the polymers can be fine tuned by altering the chemical composition of the side chain group which opens up many commercial opportunities.

Urethanes, again with varied chemical compositions, can be polymerised to produce poly(urethane)s which are bulk plastics with uses varying from impact protection to cushioning and structural components. A German consortium including a CO<sub>2</sub> source (RWE), alternative energy suppliers (Siemens) and a polymer manufacturer (Bayer) have received €118M in funding to take CO<sub>2</sub> to poly(urethane) production on a commercial scale in a process referred to as DREAM chemistry (Peters, *et al.*, 2011).

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## 4.4 Innovation in CO<sub>2</sub>-chemical conversion processes

### 4.4.1 Catalysis

Key to the success of processes to convert CO<sub>2</sub> to valuable products is the development and use of effective and cheap catalysts. It is important again to consider the supply chain for catalysts. Many catalysts used in a research environment are exotic and often sourced from geo-politically unstable regions. It is of paramount importance to develop catalysts that are available in large quantities and are stable under the reaction conditions so that they can be recycled over prolonged periods. Furthermore, the catalysts need to be robust and supported on a solid matrix to aid processability. Homogeneous catalysts, which are in the same liquid or gas phase as the reactants, tend to have complex ancillary ligand structures that are lost over the course of the reaction, thereby rendering the catalysts inactive for further use. It is not unreasonable to assume that a major target will be an integrated catalyst-carbon capture agent which will aid gas and product separation.

### 4.4.2 Artificial Photosynthesis

Considerable effort is being made to mimic biological systems and processes. Nature has developed methods for CO<sub>2</sub> capture and conversion to high energy molecules such as carbohydrates under extremely mild conditions. However, these are complex multi-catalyst and multi-reaction sequences that rely on chemical, photo-chemical and electro-chemical reactions within complex metabolic pathways. Recent studies have reported some success in individual photo- or electro-catalytic processes (DNV, 2011), but this is an area which shows considerable promise for future exploitation.

### 4.4.3 Photocatalysis

Photocatalysis may be regarded as an extension to artificial photosynthesis, where the range of chemical products is extended beyond carbohydrates and oxygen through the use of a variety of simple or exotic catalysts. This area of research is gaining popularity and there was an excellent recent review by Barton Cole and Bocarsly (2010) that looked at a number of processes. In its most efficient form photocatalysis would use natural sunlight to drive the process. However, by careful design of catalysts it becomes possible to tune the catalyst and reaction to different wavelengths to gain maximum efficiency. This would necessitate the conversion of renewable electrical energy into light but would ultimately allow renewable energy to be stored in a more useable form as a chemical.

### 4.4.4 Electrochemical Reduction

Electrochemical reduction of CO<sub>2</sub> requires the use of an electric current (in this case, created from a renewable energy source) to produce the required electrons. Products that can be formed include formic acid, carbon monoxide, methanol, methane and other hydrocarbons. In a modern day context it is another way in which renewable electrical energy may be converted into a more manageable form. Barton Cole and Bocarsly (2010) have reviewed electrochemical reduction processes in detail and Silvestri and Scialdone

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(2010) have reviewed some recent advances in electrochemical carboxylation. This area of CCU is particularly appealing to countries with high alternative energy capacities such as hydro-electric power and has been highlighted by Der Norsk Veritas as a viable strategy for Norway in a recent policy briefing paper (DNV, 2010). Advances in electrocatalysis are needed to provide stable, inexpensive, selective catalysts so that the full potential of electrochemical reduction can be explored (Hansen, 2011).

### 4.4.5 Energy Integration

On first inspection it would appear that reactions involving CO<sub>2</sub> are thermodynamically prohibitive. However many different reactions have been reported to occur. In addition to the use of catalysts and increased temperature is often used to facilitate reaction, but this represents a significant process energy cost. In order to reduce the carbon footprint it is essential that the required energy comes from renewable zero carbon emission sources such as solar, wind, geothermal, nuclear or hydro supplies. Energy from waste plants are also useful energy sources as it is possible to use heat and power at off-peak times while still managing waste, such as over the summer months. Chemicals from CO<sub>2</sub>, especially synthetic fuels, represent ways of storing energy at off peak times that would otherwise be wasted.

### 4.4.6 Process Evaluation

Due to the high energy expected in most conversion processes, it is expected that most processes will use alternative energy sources at times when demand is low. Indeed, it has been proposed that only by using renewable energy resources will the chemical syntheses become economically viable (VCI & DECHEMA, 2009). At the present time it is not possible to obtain detailed energy balances on processes that use CO<sub>2</sub>. The DREAM production reported by BAYER (Peters, *et al.*, 2011) is the only pilot scale CCU process to run on a scale close to commercialisation, but data on the process are not available.

Because of the variability of the energy source compared to peak CO<sub>2</sub> production, it will be necessary to store CO<sub>2</sub> for conversion at times when alternative energy are at their maximum availability. Therefore, utilisation processes need to be developed where there is minimum cost associated with start-up and shut-down. This coupled with the large volumes of CO<sub>2</sub> involved suggests that continuous flow rather than batch processing is necessary. It is also necessary to consider a whole systems approach to process design which involves supply chain management and public perception.

## 4.5 Potential Markets

Current estimates have put CO<sub>2</sub> utilisation potential at 1-7% for the chemicals sector and 10% for the fuels sector (Aresta, 2010; VCI & DECHEMA in Germany, 2009). However, this is based on a limited number of chemical reactions to give a limited number of products. As R&D progresses in new areas of catalysis and C-1 chemistry to build more complex

# Carbon Capture and Utilisation in the green economy

molecules, then it should become apparent that the market is less limited. There needs to be dialogue between the chemicals manufacturers and chemists to identify short and long term needs and to identify hiatuses in the manufacturing supply chain. If strategies can be developed to change the synthetic processes then new routes for CO<sub>2</sub> utilisation can be developed. This will then increase the potential for increased capture. In the 2005 IPCC report, the potential for CO<sub>2</sub> utilisation was summarised (Table 4.1), and later updated by Mikkelsen (2009).

Chemical Product or Application	Annual Market (Mt/yr)	Mt CO <sub>2</sub> used per Mt Product	Lifetime
Urea	100	70	6 months
Methanol	40	14	6 months
Inorganic carbonates	80	30	decades to centuries
Organic carbonates	2.6	0.2	decades to centuries
Poly(urethane)s	10	<10	decades to centuries
Technological	10	10	decades to years
Food	8	8	months to years

**Table 4.1**  
Current product identity and market (adapted from IPCC, 2005 and Mikkelsen, *et al.*, 2009).

While the urea market is at saturation point, there is potential to develop other market areas. In particular, inorganic carbonates and polymers offer scope for increased revenue generation. It is noticeable that poly(carbonate)s are missing from Table 4.1: these represent alternative materials for construction and personal protection applications. A recent Risk Management position paper (DNV, 2011) states that using a variety of carbon utilisation technologies can potentially reduce annual CO<sub>2</sub> emissions by 3.7 Gt. This equates to approximately 10% of current annual CO<sub>2</sub> emissions. A 10% replacement of building materials by CO<sub>2</sub> captured in stable minerals would reduce CO<sub>2</sub> emissions by 1.6 Gt yr<sup>-1</sup>. Incorporation of CO<sub>2</sub> into polymers could also account for a 0.4 Gt reduction with the CO<sub>2</sub> being stored in a stable matrix. Indeed, the scope for polymers containing CO<sub>2</sub> is vast as this class also includes poly esters, acrylates, methacrylates, *etc.* It is appreciated that one technology will not fit all and that an integrated approach will be required that will include catalysis, thermal, photochemical and electrochemical techniques.

## 4.6 Conclusions

There are several drivers for the adoption of carbon capture and utilisation (CCU) as a viable process technology in the chemicals and fuels sector. It is important that a whole system approach is considered and that supply chain networks are factored in. Most importantly the process needs to be economically viable for industry to take ownership of the technology.

## Carbon Capture and Utilisation in the green economy

Implementation of CCS retro-fit technology has cost and energy implications. In addition to capital expenditure on plant there are additional energy costs as a retro-fit unit reduces power station efficiency from approximately 40-45% to 30-35% (NAMTEC, 2011; DECC, 2009). It therefore represents a mitigation technology without payback.

By fitting a chemical conversion and refining plant post capture it is possible to produce products from CO<sub>2</sub> with various degrees of added value.

Studies by North (see Case Study 2) have shown that careful choice of product can pay back the initial capital expenditure on the plant (both capture and conversion), and also lead to profit. The period to profit is dependent on product demand and an ability to supply at the right level, with estimations in different systems ranging from 9 months to 10 years. However, it is clear that whole systems analysis of the different systems is required before definitive statements on payback time can be made.

The production of fuels in particular has the added benefit of potentially engaging the public in a positive sense. If the public perceive a benefit in turning waste into chemicals that preserve quality of life while at the same time aiding the environment they are more likely to be receptive of the technology.

CCU has the potential to alleviate the UK dependence on petrochemical supplies from overseas with the associated risks of supply chain security and price instability.

# Carbon Capture and Utilisation in the green economy

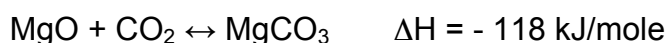
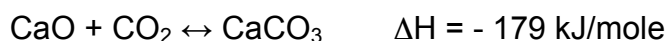
## 5 Mineral carbonation

- Mineral carbonation involves reaction of minerals (mostly calcium or magnesium silicates) with CO<sub>2</sub> to give inert carbonates. Due to the lower energy state of magnesium and calcium carbonates compared to CO<sub>2</sub>, theoretically, the process not only requires no energy inputs, but could produce energy.
- The current bottleneck, however, for a viable mineral carbonation process on an industrial scale is the reaction rate of carbonation. To enhance reaction rates, heat, pressure, chemical processing and mechanical treatment (grinding) of the mineral could be applied, but these treatments cost energy and lead to environmental impacts.
- The most realistic costs estimates for mineral carbonation through direct aqueous technologies range from 60 to 100 €/tCO<sub>2</sub> stored or 80 to 130 €/tCO<sub>2</sub> avoided. The potential, globally and in the UK, is considered very large, but the technology is in the R&D phase.

### 5.1 Introduction

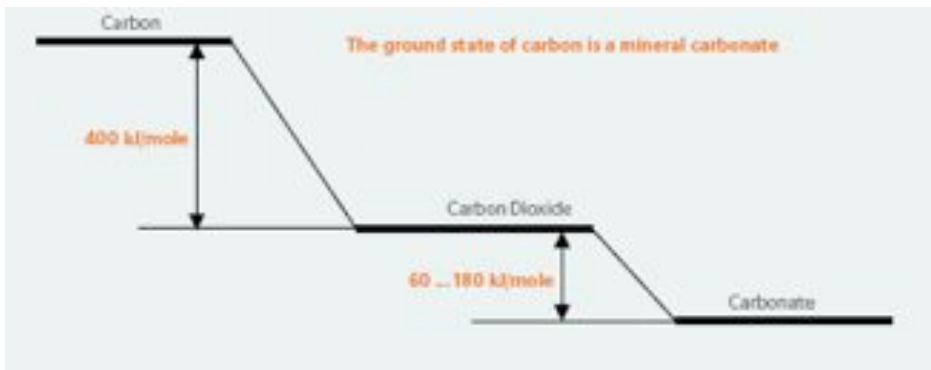
The basic idea of carbon dioxide mineral carbonation is to transform minerals (mostly calcium or magnesium silicates) with CO<sub>2</sub> into (Ca or Mg) carbonates. Magnesium and calcium carbonates have a lower energy state than CO<sub>2</sub>. Therefore, at least theoretically, the process not only requires no energy inputs, but also can actually produce energy.

The carbonation reaction can be shown by the simple reaction of binary oxides, MgO and CaO.



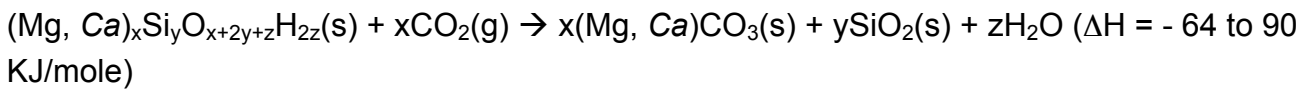
These exothermic carbonation reactions release substantial heat. For comparison, the heat released in the combustion of carbon is 400 kJ/mole.

# Carbon Capture and Utilisation in the green economy



**Figure 5.1**  
Energy states of carbon (Zevenhoven 2009).

In nature, however, calcium and magnesium are rarely available as pure oxides. They are typically found in silicate minerals. For common calcium and magnesium containing silicate minerals, the reaction is still exothermic but the heat released is less (see reaction equation below). However it will not be straightforward to use this heat effectively. The net reaction equation can be generalized as:



The main candidate minerals for carbonation are olivine, serpentine and wollastonite (see Table 5.1).



**Figure 5.2**  
Olivine (l) and serpentine (r).



Mineral type	MgO (wt%)	CaO (wt%)	R <sub>C</sub> (kg/kg)	R <sub>CO<sub>2</sub></sub> (kg/kg)
Olive	57.3	0.0	6.5	1.6
Serpentine	40 – 48		8.4	2.3
Wollastonite	0 - 1	43 - 48	13.0	2.6
Talc	34.7	0.0	7.6	2.1
Basalt	6.2	9.4	26	7.1

R<sub>C</sub> = mass ratio of rock needed for CO<sub>2</sub> fixation to carbon burned.

R<sub>CO<sub>2</sub></sub> = corresponding mass ratio of rock to CO<sub>2</sub>

**Table 5.1** Composition of various minerals and their carbonation characteristics (Huijgen, 2007)

# Carbon Capture and Utilisation in the green economy

## 5.2 Process routes

Binding carbon dioxide in carbonates can be achieved through various process routes ranging from the most basic accelerated weathering of limestone to advanced multi step processes. There are two main process routes for mineral carbonation (See figure 5.3) *i.e.* the direct route and the indirect route.

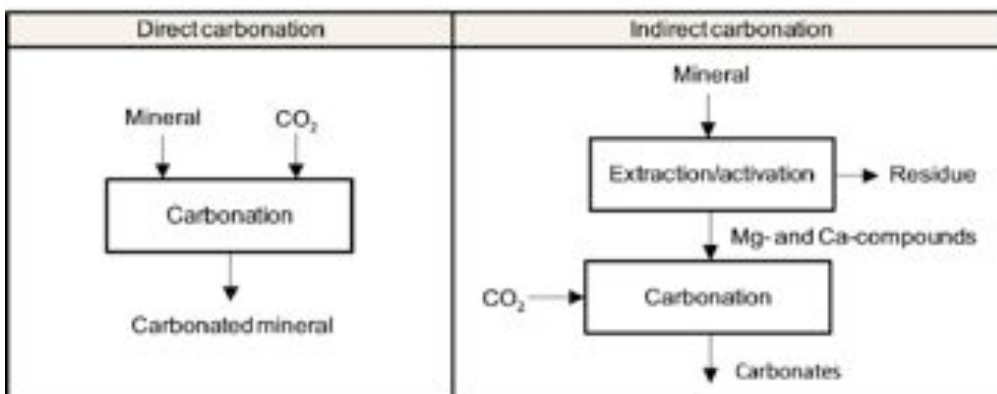
Direct carbonation is the simplest approach to mineral carbonation and the principal approach is that a suitable feedstock, *e.g.* serpentine or a Ca/Mg rich solid residue is carbonated in a single process step. For an aqueous process this means that both the extraction of metals from the feedstock and the subsequent reaction with the dissolved carbon dioxide to form carbonates takes place in the same reactor.

Dry and wet processes differ in certain aspects. The reactions in an aqueous environment are faster, but, because of the high degree of dilution and the lower reaction temperature, the heat of the (exothermic) reaction cannot be easily applied for practical purposes. In the dry process design the heat of reaction is available usefully. The reaction kinetics, however, are too slow at thermodynamically allowed temperatures.

If the process of mineral carbonation is divided into several steps it is classified as indirect carbonation. Indirect carbonation means that the reactive component (usually Mg or Ca) is first extracted from the feedstock (as oxide or hydroxide) in one step and then, in another step, it is reacted with carbon dioxide to form the desired carbonates.

In the case that the production of valuable carbonates like carbonates for paper application is the objective, an indirect or a multi staged process is also needed to remove all kinds of contaminants from the desired product  $\text{CaCO}_3$ .

In the past 4 to 5 years almost 20 patents have been have been filed concerning new innovative routes for mineral carbonation. Many of these routes are quite complex and will not be described in this paper.



**Figure 5.3**  
Direct (l) and indirect carbonation process (Zevenhoven, 2009).

# Carbon Capture and Utilisation in the green economy

Huijgen (2005) and Sipilä (2008) concluded that the direct “single” step aqueous mineral carbonation-route is the most promising and the most developed CO<sub>2</sub> mineralisation process route to date. High carbonation ratios and acceptable reaction rates have been achieved in lab scale test rigs. However, despite more than twenty years of development work, the technology has yet to reach the pilot stage due to poor economic feasibility of the process to date. Nevertheless, the direct aqueous route will be used to assess the technical feasibility of mineral carbonation as an alternative use for CO<sub>2</sub> or as an alternative for geological storage of CO<sub>2</sub>.

The current bottleneck for a viable mineral carbonation process on an industrial scale is the reaction rate of the carbonation reaction. Natural mineral carbonation (weathering) proceeds on a geological time scale due to the low reactivity of the minerals with CO<sub>2</sub>. Therefore, reaction rates must be enhanced by order of magnitude. This can be done by using heat, pressure, as well as chemical and mechanical treatment of the mineral. In addition, the reactivity of the minerals varies from case to case. For the different minerals, enhancement pathways tend to be very specific. There is a variety of pre treatment options for the minerals. The most important are:

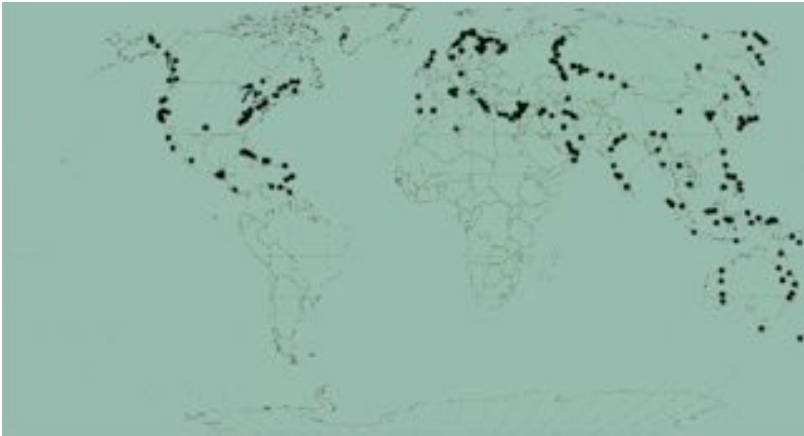
1. Size reduction *i.e.* crushing and grinding, reducing size of reduction of the mineral particles enhancing the reaction rate.
2. Magnetic separation to remove the iron (magnetite). The oxidation of iron slows down the carbonation as a layer of iron oxide is formed on the surface of the mineral particle.
3. Thermal or heat treatment. By heating the serpentine mineral particle up to 600°C bound water is removed and an open structure (higher porosity) is created improving the reaction rates.

## 5.3 Mineral resources/reserves

The most suitable feedstock minerals are olivine, serpentine and wollastonite (see Table 5.1). At many locations worldwide large deposits of olivine and serpentine are available. The magnesium-based silicate (olivine, serpentine) minerals give by far the highest capacity for CO<sub>2</sub> storage. Large deposits are available in Finland, eastern Australia, Portugal and USA.

Based on current understanding, reserves of the suitable minerals are unlikely to be a limiting factor for large scale application of mineral carbonation as an alternative for geological storage.

# Carbon Capture and Utilisation in the green economy



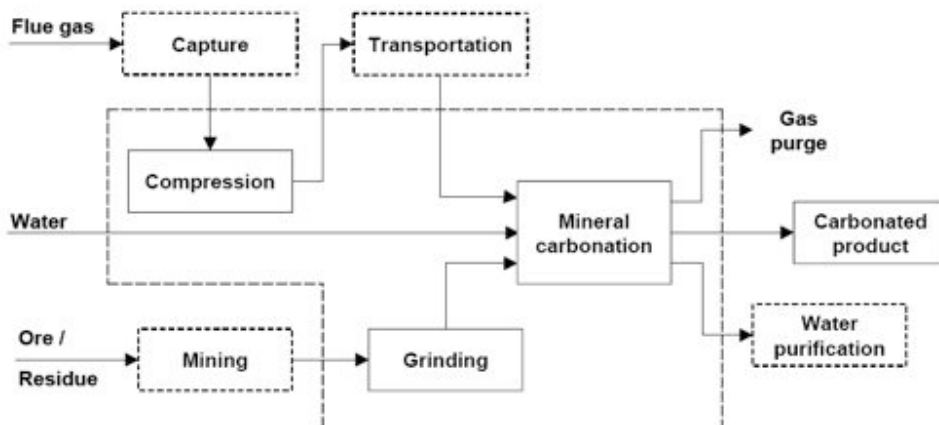
**Figure 5.4**  
Distribution of magnesium silicate mineral deposits worldwide (Lackner, 1997).

Besides natural reserves, various calcium containing industrial waste products (e.g. steel slag, cement-kiln dust, waste concrete and coal fly ash) have been suggested and tested as alternative Ca/Mg resource for carbonation. Often these materials are already appropriately sized, eliminating the cost associated with size reduction necessary for the mined mineral ore. The use of these materials would likely be in niche applications where waste could be remediated by carbonation. Even though their total amounts are too small to substantially reduce CO<sub>2</sub> emissions (potential few hundred Mt/yr), they could help introduce the technology. Although, the use of these alternative materials has been investigated more intensively over recent years, most attention has still been given to the development of appropriate carbonation processes for olivine, serpentine and wollastonite. Finland has an estimated storage capacity of 2.5-3.5 Gt using the serpentines whereas the USA has an estimated potential to store the total US CO<sub>2</sub> (current level of ca. 7 Gt/yr) emissions for more than 500 years.

## 5.4 Process evaluation

A simplified process block diagram for the direct aqueous carbonation is given in [Figure 5.5](#) below (Huijgen 2007). Captured CO<sub>2</sub> from power plant is dried and compressed to pipeline pressure and transported to the carbonation facility. CO<sub>2</sub> is dissolved in a slurry of water and mineral reactant. The CO<sub>2</sub> reacts with water to form carbonic acid (H<sub>2</sub>CO<sub>3</sub>), which dissociates to H<sup>+</sup> and HCO<sub>3</sub><sup>-</sup>. Reaction of the carbonic acid with the mineral consumes most of the H<sup>+</sup> and liberates equivalent amounts of cations and bicarbonate (HCO<sub>3</sub><sup>-</sup>), which react to form the solid carbonate mineral. Optimum process conditions for olivine, serpentine and wollastonite are summarised in Table 5.2.

# Carbon Capture and Utilisation in the green economy



**Figure 5.5** Block diagram for a direct, aqueous mineral carbonation process. System boundaries used for the calculation of the energy requirements and the CO<sub>2</sub> efficiency are indicated by the broken lines.

Mineral type	Temperature (°C)	CO <sub>2</sub> pressure (atm)	Aqueous solution	Carbonation (1 h %)
Olivine	185	150	0.64 M NaHCO <sub>3</sub> , 1 M NaCl	49
Wollastonite	100	40	Distilled water	82
Serpentine	155	115	0.64 M NaHCO <sub>3</sub> , 1 M NaCl	74

**Table 5.2** Optimum carbonation process conditions for three minerals

## 5.4.1 Solid flows and environmental aspects

Using olivine, which has the highest concentration of magnesium, 1.6 tonnes of olivine is needed to fix 1 tonne of CO<sub>2</sub>, producing 2.6 tonnes of carbonated product to be handled. In serpentine the magnesium concentration is lower, and typically 2.3 to 3.6 tonnes of serpentines is needed to fix one tonne of CO<sub>2</sub> resulting in 3.3 to 4.7 tonnes of solid material (IPCC 2005).

Mineral carbonation of the CO<sub>2</sub> emissions from a 600 MWe coal fired power plant, approximately 4 Mt CO<sub>2</sub>/yr, will result in a mining activity 6 to 8 times bigger than the coal mining activity needed for a power plant of the same size. Many Mg-silicate rocks contain iron. Large amounts of iron oxides are obtained when these materials are being mined for mineral carbonation.

It has been suggested, that magnesium carbonate and silica may find uses as soil enhancers, road fill, construction work or filler for mining operations. However, once mineral carbonation has grown to its full potential it will saturate any potential market for application of the products. Therefore, it is realistic to assume that the carbonation product could only be used for refilling the mining site.

## Carbon Capture and Utilisation in the green economy

It is obvious that the scale of these solid handling operations leads to concern over the environmental impacts and economics of mineral carbonation process as an alternative for CO<sub>2</sub> geological storage.

Name /Location	Mining activity	Ore mining Mt/yr
Escondida/Chile	Copper	374
Morenci/USA	Copper	256
Antamina/Peru	Copper, zinc	123
Venetia/South Africa	Diamond	70
Several places /World	Olivine	8
UK	Coal	18

**Table 5.3**  
Examples of mining ore activities and olivine around the world (Sipila, 2008).

In a review by the IEA Greenhouse Gas R&D Programme (IEA 2000) the environmental issues were addressed, concluding that “the methods” for mineral sequestration of carbon dioxide present significant potential for adverse environmental impacts, which are comparable with the issues faced by similar sized modern quarrying/mining operations. Once the carbon has been stored through mineral carbonation, there are virtually no emissions of CO<sub>2</sub> due to leakage.

### 5.4.2 Energy requirements and CO<sub>2</sub> efficiency

The energy requirements, based on R&D processes, for the actual mineral carbonation process for using serpentine are 3.6–8.8 MJ/kg of CO<sub>2</sub> stored and 2.3–2.4 MJ using olivine. For Wollastonite, Huijgen (2007) calculated a CO<sub>2</sub> or “sequestration” efficiency of 75%. These energy and CO<sub>2</sub> efficiency figures do not include the energy requirement for capturing the CO<sub>2</sub> from the power plant, calculated at 300 kWh per tonne of CO<sub>2</sub>, or the additional CO<sub>2</sub> emissions associated with meeting the energy requirement.

# Carbon Capture and Utilisation in the green economy

The CO<sub>2</sub> emission of a state of the art coal fuelled power plant is approx 4 Mt/yr. Such power plant operates with an average efficiency of 43% resulting in a CO<sub>2</sub> emission of 783 g/kWh. With a post combustion CO<sub>2</sub> capture plant 85% of the CO<sub>2</sub> i.e. 3.4 Mt/yr will be captured. As result the efficiency of the power plant will drop to about 33% due to the energy requirement for the capture process of 300 kWh/tonne of CO<sub>2</sub> captured. (The specific CO<sub>2</sub> emission is reduced to 145 g/kWh resulting in an avoidance rate of 82%).

For the mineral carbonation of CO<sub>2</sub> most of the energy is needed for grinding of the feedstock *i.e.* 280 kWh of CO<sub>2</sub> fixed. In total (300 + 280) 580 kWh is needed for capture and carbonation. The plant efficiency is reduced to 23.6% and the resulting CO<sub>2</sub> avoidance rate is 72.5%.

To fix 3.4 MtCO<sub>2</sub>/yr using serpentine typically 7.8 Mt/yr is needed resulting in a product stream of 11.2 Mt/yr. For mineral carbonation of 85% of the yearly CO<sub>2</sub> emission of a coal fuelled power plant in total (7.8 + 11.2) = 19.0 Mt of solid material needs to be handled.

Moreover, the power plant capacity is reduced with 45% whereas the specific energy input needed to produce one kWh is almost doubled.

For comparison the total amount coal mined in the UK in 2008 amounts 18.1 Mt. In the same year in total almost 100 Mt of crushed rocks was produced (BGS 2011).

Mineral carbonation for a new 600 MWe coal power plant. Energy requirements and CO<sub>2</sub> efficiency.

## 5.5 Costs for carbonation

There are large differences in the estimated costs of the various carbonation routes. For the most realistic direct aqueous technologies, the cost falls into a range from 60 to 100 €/tCO<sub>2</sub> stored/fixed (Huijgen 2007). Taking into account the CO<sub>2</sub> efficiencies *i.e.* additional CO<sub>2</sub> emissions associated with the required energy for the carbonation process this lead to a cost range from 80 to 130 €/tCO<sub>2</sub> avoided.

For comparison, the costs for geological storage is estimated to be in a range of 3 to 10 €/tCO<sub>2</sub> (IPCC, 2005). The permanent and safe “storage” of CO<sub>2</sub> by mineral carbonation may justify higher costs than those of geological storage but further cost reductions are required, particularly in view of (current) prices of CO<sub>2</sub> emission rights within the EU emissions trading scheme.

## Carbon Capture and Utilisation in the green economy

The cost for capturing CO<sub>2</sub> from a power plant is estimated to be in the range of 50 to 100 €/tCO<sub>2</sub> avoided so in a full CCS system with mineral carbonation this would mean that the total cost could be above 150 € per tonne of CO<sub>2</sub> avoided. For the processes that use the flue gasses directly no capture is needed and CO<sub>2</sub> avoidance costs for mineral carbonation will fall in the range given by Huijgen, *i.e.* 60 to 100 €/tCO<sub>2</sub>.

## 6 Conversion of CO<sub>2</sub>: algae

- The cultivation of microalgae in open ponds or photobioreactors could be an option for direct capture and utilisation of concentrated CO<sub>2</sub> emitted from power plants.
- Microalgae have several features that enable sustainable production concepts including high biomass productivity per unit area compared to most terrestrial crops, growth on non-arable land using salt water, waste streams as nutrient supply and flue gases as CO<sub>2</sub> source. Per tonne of algae biomass ca. 0.5 tonne of carbon (from 1.8 tonnes of CO<sub>2</sub>) can be fixed and converted to valuable products including bio-oils and proteins, high value chemicals and ingredients, food and feed, fertilizers and fuels.
- At the current stage of development the technology is not yet ready for commercial implementation. The main challenge is to achieve large-scale algal production at competitive costs. Significant RD&D and investments are required for the technology to become economically viable. For algal fuel production the main objectives are to reduce production costs and energy requirements of cultivation and processing.

### 6.1 Cultivation systems, harvesting, CO<sub>2</sub> supply

Cultivation of microalgae takes place in open-pond systems or in (semi) closed photobioreactors to which water, nutrients and CO<sub>2</sub> are supplied. Continuous mixing is needed to expose all algae cells in the system to light and to promote gas exchange. High Rate Algal Ponds (HRAP) or "raceway ponds" are the most common method for commercial algae production today. HRAP's can be built at relatively low costs (ca. 10 USD/m<sup>2</sup>) and can be easily scaled up. The culture is mixed by a paddle wheel at moderate energy costs (Fig. 6.1). A major drawback is that large-scale open systems do not allow stringent process control which limits productivity. Furthermore the relative ease of contamination limits the number of species that can be successfully cultivated in open systems. Also care must be taken to minimize the amount of CO<sub>2</sub> outgassing to the air by the choice of CO<sub>2</sub> supply system and careful dosing of the CO<sub>2</sub>.

## Carbon Capture and Utilisation in the green economy



**Figure 6.1** Photobioreactors for algae cultivation. Left: High Rate Algal Ponds, Earth Rise Farms, USA. Right: Tubular photobioreactor developed by IGV, Potsdam, Germany.

(Semi)closed photobioreactors (Fig. 6.1) offer a controlled environment which permits cultivation of algal species that cannot be grown in open systems and may attain higher productivities than ponds (Pulz, 2001). Drawbacks at the current stage are the ca. 10-fold higher investment costs ( $> \text{USD } 100 / \text{m}^2$ ) compared to open systems and the fact that scale up is hampered by engineering issues relating to gas/liquid mass transfer, prevention of wall growth and energy efficient mixing and cooling of the culture. Some recent developments addressing these issues are discussed here. HR BioPetroleum (<http://www.hrbp.com/index.html>) developed a low-cost hybrid system comprising photobioreactors and a large open pond area. Results at pilot scale show that selective cultivation is possible at a high yield and reduced costs. Algal oil production cost in a full scale system was estimated at US\$84/barrel (Huntley and Redalje, 2006).

Another development is the use of vertical flat-panel reactors (Fig. 6.2) made from thin polyethylene film, which substantially reduces investment costs. It is likely that many systems will be developed based on these design principles with expected improvements in material lifetime (and thus costs) and energy requirement for cooling and mixing (Wijffels & Barbosa, 2010; Tredici 2010).

# Carbon Capture and Utilisation in the green economy



**Figure 6.2** Development of low-cost, flat panel photobioreactors from (left) Proviron, Belgium, and (right) Solix Biofuels, USA. From: Wijffels & Barbosa, 2010.

Research has shown that flue gas from coal and gas fired power plants are suitable CO<sub>2</sub> sources for algal growth (Benemann, 1997, 2003). Also the removal of NO<sub>x</sub> and its use as a nutrient (after conversion to nitrate) for algal growth is feasible (Nagase *et al*, 1997). Possibilities also exist to utilize residual heat from flue gas for maintaining the culture temperature at optimum value to raise productivity.

Because the produced algal suspension is quite dilute, the costs for concentration and dewatering of the algal biomass may amount to 20-30% of overall production costs (Fernandez *et al*. 2003). Employed technologies include centrifugation, flotation or membrane filtration, that are relatively costly and energy intensive. The development of reliable low-cost harvesting technology with low energy consumption is one of the main challenges in the field.

## 6.2 Energy balance of CO<sub>2</sub> capture by algae

The current energy balance of algae production is less favourable than of terrestrial crops due to the high energy requirements for mixing of the culture and for harvesting and drying of the algal biomass. Muylaert & Sanders (2010) calculated a primary energy input of producing fractionated and dried algal biomass (with an inherent energy value of 21.8 GJ/tonne dry weight) of 9 GJ/tonne biomass (equivalent to 5 GJ/tonne CO<sub>2</sub> fixed) for raceway ponds versus *ca.* 63 GJ/tonne biomass (35 GJ/tonne CO<sub>2</sub> fixed) for a flat panel reactor. The latter is more than 10 -fold higher than for agricultural crops. The energy balance for raceways is positive but still the energy input is 3-4 fold higher than for most agricultural crops.

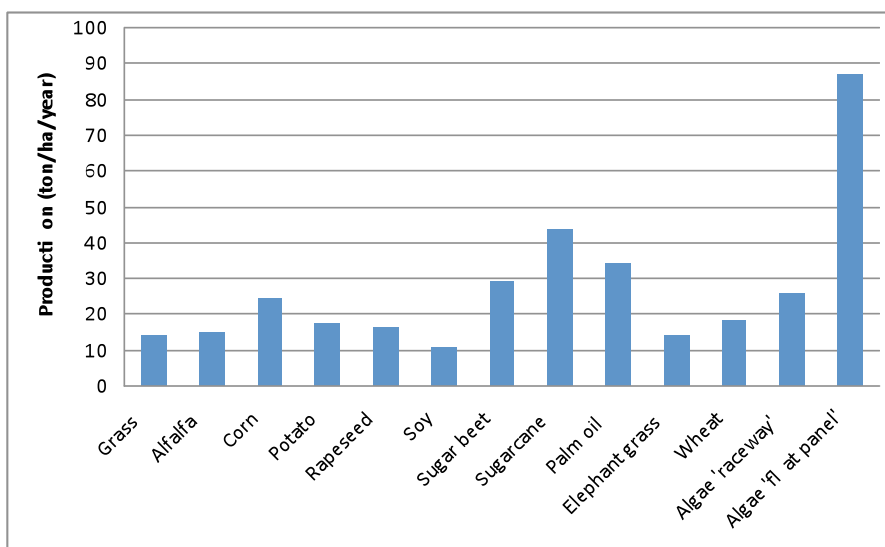
# Carbon Capture and Utilisation in the green economy

## 6.3 Productivity

A critical issue is the biomass yield that can be obtained by cultivation of micro-algae, since this largely determines the costs of the biomass. In recent years productivities exceeding 200 tonnes/ha/year have been claimed. The upper limit of productivity is determined by the maximum efficiency of photosynthesis, which is the same for algae and green plants (Tredici, 2010). For Northern European countries, such as the UK, (53° N or further north) this would imply a theoretical maximum biomass productivity of 208 tonnes dry weight/ha/year. In practice, however, the maximum efficiency is never achieved, so these optimistic projections will have to be nuanced.

The main reason for lower efficiencies and therefore lower than maximum yields are losses caused mainly by biological limitations. In open systems in the Netherlands, 26 - 35 tonne of dry biomass per ha/year can be reached (Muylaert & Sanders, 2010). Bowles (2007) reports average biomass yields in commercial raceway ponds between 10 and 30 tonne/ha/year with the highest reproducible productivities at 50-60 tonne/ha/year. This is comparable with yields in tropical agriculture. For algae higher values can be observed under controlled conditions in short duration experiments, but these conditions cannot be transferred to commercial large-scale systems.

In a recent review, Tredici (2010) made an effort to settle the debate by stating that "biomass productivities of 80 tonne/ha/year, which are in the range of high yields attained with crops such as sugar cane in the tropics, must be considered as the maximum achievable at large scale with microalgae". This was confirmed by Muylaert & Sanders (2010), who have compared the production of algae under Dutch climatic conditions with agricultural crops (Figure 6.3). The maximum productivity of algae in a flat panel photobioreactor was estimated at ca. 80 tonnes/ha/year (see also estimates by Norsker *et al.* (2010).



**Figure 6.3**  
Productivity of agricultural crops and algae in tonnes dry matter per hectare per year. Adapted from Muylaert and Sanders, 2010.

# Carbon Capture and Utilisation in the green economy

## 6.4 Large scale CO<sub>2</sub> fixation capacity

The CO<sub>2</sub> fixation capacity of an algal system is proportional to the occupied area and the biomass productivity per hectare.

At a typical C content of 50 wt% in the algal biomass the CO<sub>2</sub> fixation capacity is about 0.5 tonne carbon from 1.8 tonne of absorbed CO<sub>2</sub> per tonne of biomass (dry weight basis).

The fixation of 1/3 of the CO<sub>2</sub> emitted by a 600 MWe coal fired power plant *i.e.* 4 ktonnes of CO<sub>2</sub>/day during 365 days per year or 1.46 Gtonnes of CO<sub>2</sub> per year would require an algae cultivation surface of about 10 kha (*ca.* 100 km<sup>2</sup>) assuming a productivity of 80 tonnes dry biomass/ha/yr. The amount of algal biomass produced would be on the order of 800 ktonnes.

Van Harmelen and Oonk (2006) see a potential for algal CO<sub>2</sub> fixation in particular in warmer and sunnier regions, with near term applications in combination with waste water treatment and fertiliser recycle and production. In the midterm (15-20 years) they expect that processes might be developed by integrating biofuels production with higher value/large market co-products such as biopolymers and animal feed. In the longer term single purpose algae biofuels production may become feasible (Van Harmelen and Oonk, 2006).

## 6.5 Products/markets and economics

The current global micro-algae production is close to 10 ktonnes of dry biomass/yr. The main applications for algal products comprise high-value applications in food supplements, aquaculture feeds and ingredients for food and cosmetics with an estimated retail value of US\$ 5-6.5 billion per year (Pulz and Gross, 2004). Potential products from algae include bio-oil (up to 40%), proteins (30-50 %), polysaccharides for the production of chemicals, bio-active products, food and feed ingredients (including omega-fatty acids), fertilizers and fuels. The feasibility of these applications depends on achievable production costs as well as the actual entry of algal products in the market.

Current prices of algae on the industrial market range from US\$ 5000 to 11000/tonne and 3750 to 7500 €/tonne for algae produced in China (Bowles 2007). Muylaert and Sanders (2010) report a production cost of algae in photobioreactors at *ca.* €10,000/tonne and project a reduction to €3,800 to 6,000/tonne due to scale factors. Norsker *et al.*, 2010, have estimated microalgae production costs for three different systems at commercial scale: open ponds, horizontal tubular photobioreactors and flat panel photobioreactors. The costs including dewatering, were estimated at €4.95, 4.15 and 5.96/kg, respectively. *Via* optimization of the most important cost drivers, a price of €0.68/kg (€680/tonne) could be

# Carbon Capture and Utilisation in the green economy

reached. At this cost level algae may become a viable feedstock for biofuel and bulk chemicals.

Evidently, lowering of the production costs and increasing the value and revenues of (co)products are central elements in any optimization effort. There are a number of algal products with a high market value e.g. omega fatty acids, but their market volume is incompatible with the market for biofuels and CO<sub>2</sub> fixation. More market compatible products could include fertilizers, inputs for the chemical industry and alternative paper fibre sources (van Iersel, 2010).

## 6.6 Fuel from algae

At present there is a renewed interest for the concept of using oil accumulating algae to produce biofuels (Sheehan *et al.*, 1998). Substantial investments have taken place recently in this sector in public-private partnerships e.g. Chevron-NREL, DARPA-UOP, and private companies. These investments are justified by the high potential that algae offer for production of vegetable oils compared to alternative oil crops (Table 6.1). In addition the algae cultivation systems do not require use of arable land and valuable fresh water sources.

Crop	Oil yield (L/ha)	Land area needed (Mha) <sup>a</sup>	Percent of existing US cropping area <sup>a</sup>
Corn	172	1540	846
Soybean	446	594	326
Canola	1190	223	122
Jatropha	1892	140	77
Coconut	2689	99	54
Oil palm	5950	45	24
Microalgae <sup>b</sup>	136,900	2	1.1
Microalgae <sup>c</sup>	58,700	4.5	2.5

**Table 6.1**  
Comparison of some sources of vegetable oils.  
(Source: Chisti, 2007)

<sup>a</sup> For meeting 50% of all transport fuel needs of the United States.

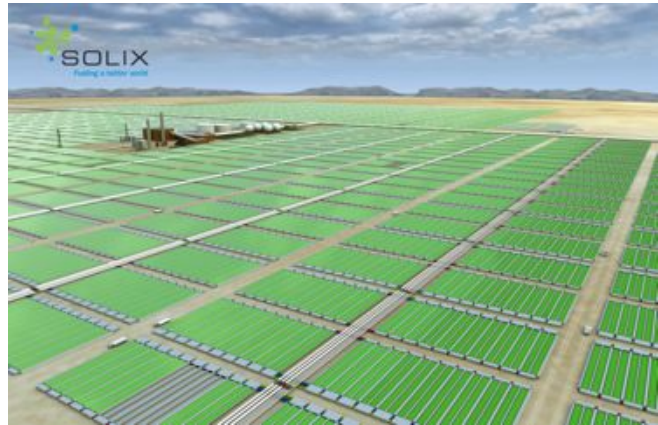
<sup>b</sup> 70% oil (by wt) in biomass.

<sup>c</sup> 30% oil (by wt) in biomass.

Various companies – mostly in the US – are active in the development of fuels from algae including Solix Biofuels <http://www.solixbiofuels.com/>, Origin Oil <http://www.originoil.com/> Sapphire Energy <http://www.sapphireenergy.com/> and HR Biopetroleum <http://www.hrbp.com/index.html>.

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Most companies focus on the production of drop-in fuels from oil rich algae e.g. for aviation. A current trend in the industry is the co-production of bio-fuels and suitable co-products (e.g. proteins, green chemicals, biopolymers) to improve economics (Thurmond, 2011). In Australia companies Aurora Algae and Algae Tec are active in the field of algal fuels production and other products (Lane, 2011).



**Figure 6.4**  
Impression of a future algae fuel farm.  
(Source: Solix Biofuels)

According to Wijffels and Barbosa (2010) the biomass cost could be reduced to €4/kg by scale enhancement. By making use of residues including waste water and CO<sub>2</sub> from flue gas, and technological improvements the price could reduce 10-fold to €0.40 /kg. For feasible production of biofuels the whole algal biomass would have to be utilised, consisting roughly of 50% oil (valued at €0.40/kg), 40% proteins (€1.20/kg) and 10% sugars (€1.00/kg). This biorefinery approach causes the biomass value to rise to €1.65/kg which would be sufficient for commercial fuels production.

## 6.7 Future perspectives

Algae have a number of features that enable sustainable production concepts. This includes high biomass productivity, the possibility of utilizing marginal, non-arable land, salt water, waste streams as nutrient supply and flue gases as CO<sub>2</sub> source to produce fuels and a range of non-fuel products. Furthermore algae can attain much higher oil and protein yields than traditional crops.

The main challenges for a meaningful contribution of algal CO<sub>2</sub> biofixation are to achieve large-scale algal production at competitive costs. Considering technology readiness we can conclude that today technologies are not yet available for commercial implementation at large-scale and that significant R&D and investments are required for the technology to become economically viable.

For fuel production the main objectives are to reduce production costs and energy requirements while maximizing lipid productivity and to increase the biomass value by making use of all algal biomass components *via* a biorefinery approach. For the near term combinations of CO<sub>2</sub> biofixation with waste water treatment and fertilizer production are a distinct possibility.

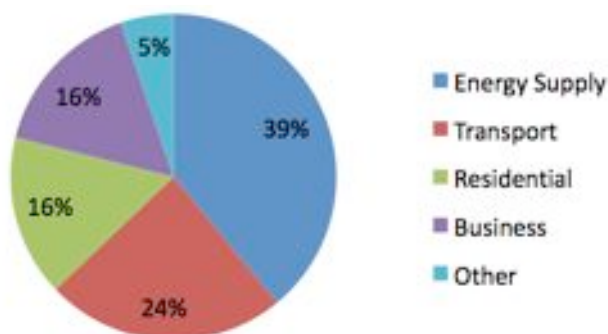
# Carbon Capture and Utilisation in the green economy

## 7 International context

### 7.1 United Kingdom

#### 7.1.1 Meeting climate targets

The UK emits more than 470 million tonnes of CO<sub>2</sub> per year and of this 39% is emitted by the energy sector (Fig 7.1 DECC, 2009 emission figures). The main strategy in the UK to reduce the amount of CO<sub>2</sub> emitted by the energy sector is to fit post-combustion carbon capture units to fossil fuel power stations.



**Figure 7.1**  
Sources of carbon dioxide emissions in 2009.  
DECC 2010.

A study by the British Geological Society (1996) estimated that the UK has the capacity to store in excess of 7.5 Gtonnes of CO<sub>2</sub> in offshore oil and gas fields. This equates to storing approximately 15 years worth of the total UK CO<sub>2</sub> emissions. The potential for further storage in saline aquifers would further increase the capacity for CO<sub>2</sub> storage and would solve the problem of CO<sub>2</sub> emissions in the short term.

CCU can be seen as an alternative to CCS, however practically it will not allow for the sequestration of CO<sub>2</sub> at the required levels to meet the UK CO<sub>2</sub> reduction commitments. Current estimates calculate that about 7% of the emitted CO<sub>2</sub> could be converted into chemicals in the short to medium term. However this figure could be much larger if efficient methods of producing fuels are developed (Aresta, 2010). CCU may however, help to reduce the UK's dependence on fossil fuels to create valuable commodity chemicals, intermediates, fuels and other products.

#### 7.1.2 Contribution to energy security

A reliance on foreign oil imports, particularly from geopolitically instable regions, and the volatility of the crude oil market has the potential to severely disrupt the sustainable recovery of the UK economy. CCU has the potential of easing our dependence on crude oil by creating alternative pathways (chemical or biological) to synthesising products, such as substitutes for transportation fuel.

Utilising the CO<sub>2</sub> captured by carbon capture units for algal growth, chemical feedstocks or mineral carbonation, may help overcome investment barriers due to the high investment costs associated with capture equipment. Currently in Europe, the only long-term incentive to capture carbon is provided through the EU ETS, however for the foreseeable future it is doubtful whether the price per tonne of carbon abated will reach levels high enough to stimulate CCS beyond a demonstration phase.

# Carbon Capture and Utilisation in the green economy

CCU enables the recovery of initial and running costs by using the CO<sub>2</sub> as a valuable commodity, and such technologies have the potential to complement CO<sub>2</sub> storage pathways. For example, a power plant combined with both CCS and CCU could theoretically select a CO<sub>2</sub> pathway dependent on market dynamics (*i.e.* price of EU ETS vs. synthetic fuel price).

Studies at Newcastle University on a CCU plant creating cyclic carbonates calculated a payback time of under 2 years and a profit in excess of £1.4 billion over 15 years if the carbonates were sold at current market prices (Case Study 2). These costs include construction and operation of the utilisation and refining plant, using CO<sub>2</sub> directly from the flue gas.

Another possible advantage of the UK investing in CCU research and development could be the ability to export the technology to the rest of the world. Whereas the UK has a substantial amount of geological storage for CO<sub>2</sub>, there are many countries in the world not in the same position. In these countries the opportunities of CCU provide a method of reducing CO<sub>2</sub> emissions without the problems that would arise from the lack of suitable geological storage.

## 7.1.3 Improving public perception

There are a number of challenges surrounding the public's perception of CCS in the UK. Gough and Shackley (2006), at the Tyndall Centre for Climate Change Research stated that these problems were:

- a) the relatively technical and 'remote' nature of the issue, meaning that there are few immediate points of connection in the lay public's frame of reference to many of the key concepts;
- b) the early stage of the technology, with very few examples and experiences in the public domain to draw upon as illustrations.

Their findings revealed that in their survey group, support for CCS is most appropriately described as moderate or lukewarm compared to strong support in general for wind, solar and energy efficiency. They also found there was a reasonable level of consensus surrounding the potential need for CCS given the scale of the decarbonisation challenge and the uncertainty and difficulty of achieving a 60% reduction in emissions through behavioural and lifestyle change and other routes. Support for CCS was conditional upon the implementation of a range of other decarbonisation options: in particular renewable energy and energy efficiency (Gough & Shackley, 2006). If communicated correctly, when presenting the public with options surrounding CCS, CCU may be seen in a favourable light, as the economic and supply chain benefits of creating valuable products rather than storing the CO<sub>2</sub> are apparent.

# Carbon Capture and Utilisation in the green economy

Furthermore, accelerated mineralisation offers the opportunity to either deposit the product underground as a storage option or to utilise it in the construction industry, contributing to the built environment and mitigating some of the emissions associated with concrete and clinker production. If the public perception of CCS using geological storage changes to be overwhelmingly negative; the option of using mineral carbonation could become more attractive. However due to the high costs of using mineral carbonation just as a storage option (*i.e.* not for the production of aggregates and cements that could be sold), the use of mineral carbonation in the UK is only likely to be viable if storage in geological formations is unavailable.

## 7.2 European Union

Mineral carbonation in the European Union could be of interest for those countries that have limited geological storage capacities either on- or offshore. Finland is an example of such a country, as well as Portugal, Greece, Hungary, Lithuania and countries in the Baltic region where saline aquifers are less suitable for CO<sub>2</sub> storage. An interesting niche market for the European union is the carbonation of alkaline waste materials like blast furnace slag and fly & bottom ash. This could be very attractive for European steel plants, where 1 tonne of slag can capture 250 kg of CO<sub>2</sub>. However this would only reduce the steel mill emissions by 1.5%. An additional benefit is that the quality of the carbonated steel slag would be improved.

Mineral carbonation will involve handling vast amounts of solids, and demands an infrastructure capable of handling such high volumes. Mineral carbonation will be restricted to those regions in Europe with a good infrastructure for bulk goods. Typically harbours like Rotterdam (almost 400,000 metric tonnes per year) and Antwerp have terminals equipped for bulk solid handling. The economic feasibility of this route depends on the value of the specific carbonate minerals and needs to be further researched.

Large scale fixation of CO<sub>2</sub> with algae demands a large cultivation surface. Typically for a 600 MW coal fuelled power plant at least 200 km<sup>2</sup> is needed to fix the CO<sub>2</sub> emissions. So this route for use of CO<sub>2</sub> use would fit more in the rural regions of Europe where (farming) land could be used for algal biomass. As a consequence, CO<sub>2</sub> needs to be transported to these areas.

# Carbon Capture and Utilisation in the green economy

## 7.3 Outside the European Union

### USA

CCU is viewed in the USA as an important technology. Announcing US\$ 106 million of investment in CCU processes such as carbonation, algae capture to produce biofuels and production of polycarbonates. The US Energy Secretary stated: “These innovative projects convert carbon pollution from a climate threat to an economic resource. This is part of our broad commitment to unleash the American innovation machine and build the thriving, clean energy economy of the future”<sup>12</sup>. The perceived benefits to the US economy are clearly recognised and alongside investment in CCS, there has been investment in CCU processes. Due to its geographical, economical and scientific situation the USA has potential to use any of the processes described in this report and is currently conducting research in all of them.

### Australia

The climate and geographical situation in Australia make the country particularly suited to algal capture and utilisation. The large amounts of solar radiation plus land available and the economic benefits are driving the technology forward. MDB Energy in Australia has received AUS\$ 5 million of funding which is matched with an AUS\$ 5 million investment from the company to commercialise a bio-carbon capture and storage process at 3 major Australian power plants. The process will use algae to produce bio-oils and animal feeds which can be sold at a higher cost than operational costs. This process when at full scale on a single 80 hectare site would use more than 70 Mtonnes of flue gas emissions and produce over 11 million litres of oil, approximately enough for 18,000 cars per year (based on consumption of 1 tank of fuel per month).<sup>13</sup>

Australia also has significant activities in mineral carbonation. NSW has been found to be not well suited to geological storage and mineralisation is being investigated as an alternative. The Australian government has invested AU\$3 million into building a pilot plant for capturing CO<sub>2</sub>, mineralising it and using the product for building materials, bricks, pavers, cement and agricultural additives.<sup>14</sup>

<sup>12</sup> [http://fossil.energy.gov/news/techlines/2010/10027-DOE\\_Announces\\_Six\\_Projects\\_to\\_Conv.html](http://fossil.energy.gov/news/techlines/2010/10027-DOE_Announces_Six_Projects_to_Conv.html) Last accessed 23.03.2011

<sup>13</sup> <http://www.mbdenergy.com/catalogue/c5/p246/cp4> Last accessed 23.03.2011

<sup>14</sup> <http://scinews.com.au/releases/410/view> Last accessed 04.04.2011

# Carbon Capture and Utilisation in the green economy

## Developing economies

The application of the different processes and technologies described in this report will vary in relevance from country to country depending on a number of factors. In some countries e.g. China and India the economic benefits of CCU will be the driving force to balance the costs of traditional CCS and this is already happening (see section 3.4).

Potential suitability in other developing countries will be dependent on a number of factors such as:

Environment – geographical location, climate suitability, availability of natural resources.

Market – demand for CCU products, availability of technology, engineering expertise.

Politics – incentives to reduce CO<sub>2</sub> emissions, investment climate, trade barriers.

Some developing countries, in particular African nations, are very suitable for algae production. Large amounts of solar radiation, and land availability, particularly degraded land and deserts, provide suitable conditions. An advantage of algal production is that it can use saline or brackish water so there is no requirement for fresh water sources.

The market for a specific product might be the driving force in other areas. Aggregates and cements produced using CO<sub>2</sub> and fly-ash from power plants will be useful products in countries with large amounts of construction taking place.

## 8 Recommendations to policymakers

### 8.1 International policy context

If there are possibilities for CCU in specific countries, it is important that they are advanced without inhibiting appropriate deployment of conventional CCS or other mitigation options and energy technologies. Synergies between conventional carbon capture, microalgae production and CO<sub>2</sub> as a chemical feedstock are apparent and should be pursued. Geological storage and mineral carbonation may both be viable and could possibly be applied sequentially when storage capacity runs out or when public perception issues arise.

Policymakers have several options to advance carbon capture and utilisation technology. First, as most options around CCU are still in the R&D phase, it makes sense to first exchange and build up knowledge in a global network. For biofixation this has been done in the past in a network under the IEA Implementing Agreement IEA GHG R&D Programme. This network, however, was ended in 2009<sup>15</sup> as the IEA GHG R&D Programme focuses entirely on conventional CCS options. A concrete possibility is to **form a separate IEA Implementing Agreement** on CCU<sup>16</sup>, involving industry, government and research organisations. The IEA GHG Network on Biofixation did result in an R&D Roadmap. The second concrete recommendation is to **initiate a Global Technology Roadmap on CCU**, which could also be done for the three options outlined above and have a global scope. It could also include regulatory, policy and public perception aspects and serve to increase the policy interest in CCU.

Potential **financial support for R&D** is most commonly given in the context of government funding, or in the European Union, but the area of CCU also attracts attention from venture capitalists and firms. These could be given **tax breaks for R&D in the field of CCU**. In the longer term, carbon standards or a carbon price or tax would have to be significantly higher than current levels in the EU Emissions Trading Scheme or the UNFCCC's Clean Development Mechanism to incentivise CCU. Eventually, a **structural economic or regulatory incentive** will be needed, but it is unclear what that is likely to be. In order to be eligible under carbon finance instruments, sound accounting of greenhouse emission reductions, including the energy demand and life-cycle aspects of the various CCU options, is needed. A place to start is the IPCC Task Group for National Inventories which prescribes **best practices for GHG accounting for national reporting** to the UNFCCC. In addition, a CCU Roadmap could recommend making preparations for accounting for the option in carbon trading mechanisms, such as the CDM.

<sup>15</sup> <http://www.ieaghg.org/index.php?/2009112028/biofixation.html>

<sup>16</sup> <http://www.iea.org/techno/ia.asp> for an overview of existing IEA Implementing Agreements

# Carbon Capture and Utilisation in the green economy

## 8.2 UK-specific recommendations

Global investment in carbon capture and utilisation is increasing with considerable investment in Germany and the USA. China is also beginning to realise that utilisation of CO<sub>2</sub> is important for their economy as well as contributing towards greenhouse gas mitigation. DECC (2010) have identified that new technologies need to be adopted in order to realise 2050 emissions targets and the UK government has also identified fuel poverty and security of supply as major issues. There has been considerable UK investment in CCS, however storage should be considered to be one solution, coupled with process emission reductions, and zero-emission technologies. By comparison to CCS and global investment in CCU, the UK's contribution is small.

There should be **research** carried out to consider the feasibility and economic benefits of CCU to the UK economy and beyond. It is important to determine which technologies are relevant to the infrastructure, geology and economy in the country. In particular we need to consider the role that synthetic liquid fuel production from chemical catalytic and algal technologies can play in reducing the UK's dependence on oil rich nations for the maintenance of energy supply. It is particularly important to carry out full energy and material balances over complete systems, including full evaluation of the role renewable fuels can play in these processes. By creating UK liquid hydrocarbon production facilities, the UK can become less vulnerable to the destabilisation of crude oil prices.

CCU offers the opportunity for investors to **profit from the production of consumer chemicals** by treating CO<sub>2</sub> as a commodity rather than as a waste product. The positive contributions that CCU can make to the economy needs to be emphasised through strategic publications. A recent article in the Royal Society of Chemistry Magazine *Chemistry World* (Extance, 2011) highlighted the benefits for CCU but failed to identify any UK research in the area, despite the RSC (2006) hosting a number of conferences on the subject and the range of research already being undertaken in the UK, particularly in universities. We therefore recommend a **comprehensive review of global technologies** that are close to or at a commercially viable stage and which are applicable to the UK infrastructure. This needs to be considered in terms of economic and technical viability. It is also important that there is also an **analysis of current UK research and development** and recommendations into what further research is required to improve the UK's competitiveness.

There is a need to **form a strategic policy group on CCU** that engages academia, industry and government. A policy needs to be implemented by which the UK can assess the commercial viability of a range of utilisation options and **set targets for CCU to run alongside CCS** that identify strategic technologies and commodities markets. Unlike CCS, there is an expectation that the public will buy into the proposed technologies as there is a tangible benefit that will affect them directly: the maintenance of quality of life. There is also

## Carbon Capture and Utilisation in the green economy

the opportunity to draw on the experiences of our European colleagues to develop these strategies.

The UK is trailing in the drive to embrace CCU principles and technologies. It is therefore important that we act now to put technologies in place to deliver us security in a post-petrochemicals era. The German Federal Government has provided a **workable and realistic model for the development of a CCU economy** (BMBF, 2009). It is our recommendation that we use this as a template to develop a UK strategy to harness the considerable scientific and engineering talent within the UK before we slip too far behind. We also propose a **UK Roadmap on CCU** to feed in to any Global Roadmaps that are developed.

We also recommend the establishment of **consultation groups** working with government departments, providing evidence into committees reporting to or formed by the OCCS, DECC and the Committee on Carbon Capture.

The *Engineering and Physical Sciences Research Council (EPSRC)* has funded a Grand Challenge Network in CCU for two years initially. The **CO2Chem Network** ([www.co2chem.com](http://www.co2chem.com)) is active in bringing together academia and industry both within the UK and globally. Once its benefit and value are demonstrated, the network should to be **extended** beyond the initial period of tenure and **expanded** to become a global focal point for discussions and collaborations with in the CCU community.

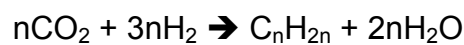
# Case Study 1

## Case Study 1: Making a carbon-neutral drop-in replacement for fossil transport fuels



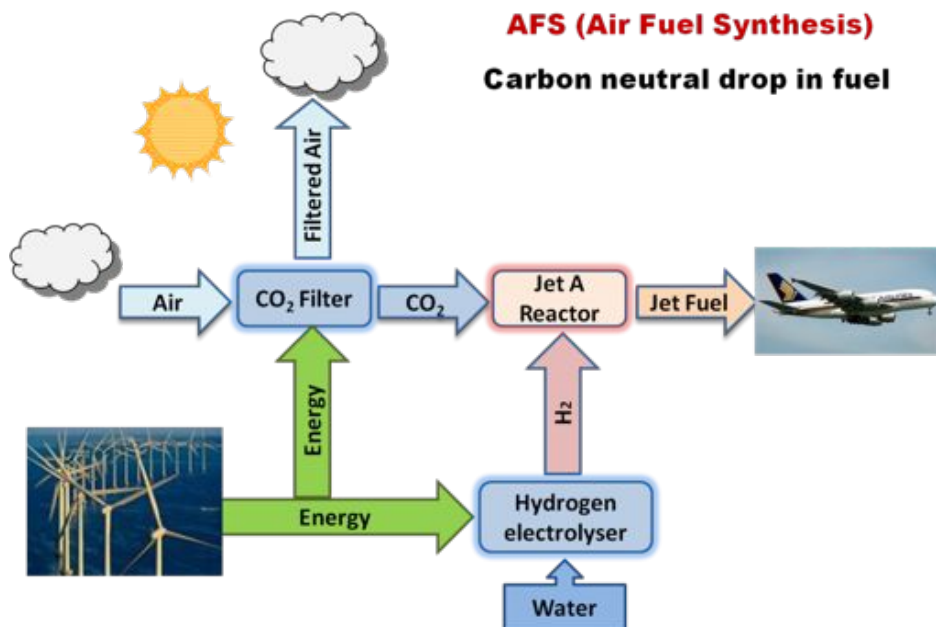
### Air Fuel Developments Ltd

The Air Fuel Synthesis (AFS) Process is a method of making transport fuels, and other hydrocarbon based products, sustainably using air as the chemical feedstock. The AFS process captures carbon dioxide from the air, electrolyses water to make hydrogen and reacts the carbon dioxide and hydrogen together to make hydrocarbon fuels as shown below:



where  $n$  is the number of carbon atoms in a long-chain or cyclic hydrocarbon.

The only other inputs required are electricity to drive the equipment in the AFS plant and the cheap, widely available chemical, sodium hydroxide. This is used to capture carbon dioxide from the air and is then recycled during the process. It is even possible to draw the water for the electrolysis process from the air. The relatively novel part of the carbon capture process is the method of releasing  $\text{CO}_2$  from solution, which uses an electrochemical cell.



If the AFS process is driven by renewable electricity then the overall process of carbon dioxide capture, fuel production and fuel combustion will be carbon neutral. Manufacture of AFS fuels is unrestricted by availability or price of raw materials, geo-politics and is unaffected by issues of land use or food availability that trouble existing biofuels.

## Case Study 1

Air Fuel Developments Ltd have funded the Centre For Process Innovation (CPI) in Teesside to commission a 5 litre per day demonstration unit. The goal is to test the theoretical system energy requirements which are currently calculated for the production of 1 litre of fuel as:

<b>Process</b>	<b>Energy requirement, kWh</b>
Carbon dioxide capture	0.44
Carbon dioxide release	4.6
Hydrogen generation	14.6
Fuel synthesis reaction	1.74
<b>TOTAL</b>	<b>21.38</b>

AFD have always argued that the technology to make these fuels is already available so the challenge is to apply these technologies to the task and integrate them. The key to the economics of the process is the availability of cheap, carbon neutral electricity. Looking at the electricity grid as a whole, it will be many years before there is a net surplus of renewable and/or nuclear power; from studying DECC's example pathways to 2050, this might not happen till the year 2030. However, there are already several locations in the UK and elsewhere that have excellent renewable energy resources, but where connection of a renewable generator to the grid is prohibitively expensive. Even when a grid connection is available, there are times and places when renewable generators, especially wind farms, have to be curtailed to ensure the stable operation of the grid. AFS provides an alternative use for these stranded renewable resources, converting renewable energy into fuels.

### Future Plans

The next stages will be to scale up to 1 tonne of fuel per day, then to hundreds of tonnes per day, at the same time as carrying out process improvement and plant automation. An early market for AFD will be remote communities with a demand for liquid transport fuels and stranded renewable energy.

- One key area of research and development will be in the catalyst and reactor design for fuel production. AFD already has a prospective partner with improved, robust catalyst materials.
- Another area of research will be in reducing the energy required for CO<sub>2</sub> capture and release. The theoretical minimum energy for extracting CO<sub>2</sub> from the air at less than 0.04% concentration and releasing it as a concentrated stream is less than 0.2 kWh per kg. However, even flue gas CCS systems, starting with a concentration of up to 15% struggle to do better than 0.5kWh per kg. We believe we can do better.

## Case Study 2

### Case Study 2: Turning waste CO<sub>2</sub> into a valuable resource

Professor Michael North



*Dymeryx*  
*Dymeryx*

Carbon dioxide is a waste product in many industries and is a major contributor to global warming and associated climate change. The only large scale solution to the problem of CO<sub>2</sub> emissions currently being considered is carbon capture and storage. However, this is an energy intensive and hence expensive process which will result in increased fossil fuel consumption and increased energy costs. A more attractive solution would be carbon capture and utilisation in which the waste CO<sub>2</sub> was not dumped, but converted into a commercially valuable product. The aim of this project was to demonstrate that waste CO<sub>2</sub> in power station flue-gas could indeed be converted into a valuable chemical for which there is a large scale demand.

Over the last four years, the North group at Newcastle have developed a new class of catalysts for the conversion of CO<sub>2</sub> into a commercially important cyclic carbonates. These have a large number of commercial applications, including:

- Electrolytes for lithium ion batteries
- Fuel additives for petrol, diesel and aviation fuel
- Polar aprotic solvents
- Chemical intermediates
- Production of polycarbonates and polyurethanes

Cyclic carbonates are currently manufactured world-wide from CO<sub>2</sub> and epoxides, but current commercial processes utilise catalysts which require pure CO<sub>2</sub> and high operating pressures and temperatures. Current commercial processes generate, rather than consume, CO<sub>2</sub>. The current global production of cyclic carbonates is around 2 Mtonne per annum, but it has been estimated that this market could increase to 45 Mtonnes per annum if the cost of their manufacture could be reduced by around 25%.

The unique feature of the Newcastle system is that the catalysts operate at atmospheric pressure and at temperatures between ambient and 100 °C, easily accessible utilising low grade heat. A spin-out company (Dymeryx Ltd) has been formed to exploit the technology. Basic research already completed has shown that the catalysts can be immobilised in a gas-phase flow reactor and that CO<sub>2</sub> concentrations as low as 5% are sufficient to allow the synthesis of cyclic carbonates to proceed. Thus, we are aiming to produce a reactor which could be retro-fitted to existing combustion based power stations to take the waste CO<sub>2</sub> directly from their exhaust gas stream (without any form of expensive carbon capture) and

## Case Study 2

convert it into chemicals, the sale of which would provide an additional income stream to the power company.

The waste  $\text{CO}_2$  produced by power stations is highly impure, containing numerous impurities.  $\text{NO}_x$  and  $\text{SO}_2$  had no effect on catalyst activity or lifetime.  $\text{SO}_3$  did have a measurable effect on catalyst lifetime although this was insignificant over the expected the catalyst lifetime.

Samples of catalyst have been exposed to real flue gas generated from the burning of natural gas or coal at Doosan Babcock's pilot plant. The real flue gas was found to have no effect on catalyst activity when the catalyst was used to produce cyclic carbonates in a gas phase flow reactor.

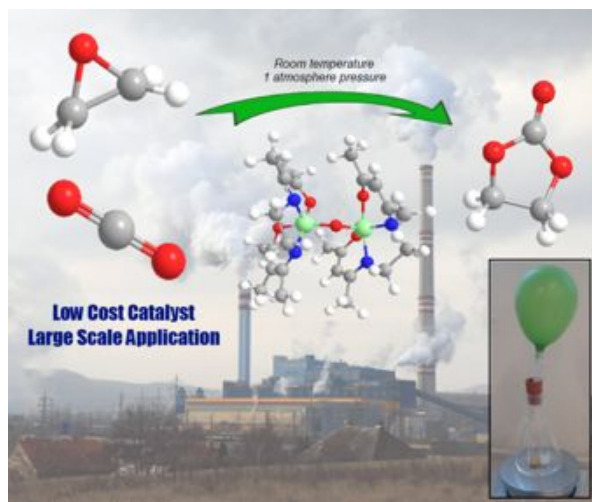
In addition to the scientific work, the economics of the process was investigated if implemented on coal or natural gas fuelled power stations. A detailed financial analysis of the process showed that if it produced just 450 Ktonne of cyclic carbonates per annum (about 25% of the current market size or 1% of the projected market size), either scenario would have a payback time of under two years and would produce a profit >£1.4 billion over 15 years at current market prices for the starting materials and cyclic carbonates. Even if the value of the cyclic carbonate was reduced to 60% of its current value, the process would still make a profit.

This project has proven that there are no problems associated with using waste  $\text{CO}_2$  in real flue gas with the Dymeryx catalysts. This technology is extremely disruptive in that it brings together two traditionally totally separate industries – power generation and chemicals production. The integrated power and chemicals production system developed in this project would offer both financial and environmental rewards if developed to full scale and will also replace carbon capture and storage with carbon capture and utilisation.

### Future work

Dymeryx is currently seeking investment to allow it to carry out further work associated with:

- Optimising the structure of the catalyst and support
- Minimising catalyst production costs
- Construction of a pilot plant



## Case Study 2

The applied research is expected to take two years followed by another two years to construct the pilot plant and prove the technology. Thus, the Dymeryx technology will be ready for full scale commercialization in about four years' time.

### Acknowledgements

This project was a collaboration between Newcastle University, Scottish and Southern Energy and Doosanbabcock and was funded by the TSB. The underlying research was funded by EPSRC, CarbonConnections and Newcastle University.

# Carbon Capture and Utilisation in the green economy

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