

Getting to know CCS



Robert Smyth, Grant Johnson and David Wilkinson, Costain Energy & Process, UK, present an overview of developments in carbon capture and storage.

It is now generally accepted that climate change is being caused by human activities and will continue if left unchecked, causing irreversible effects on the environment and human society.

Action to reduce greenhouse gas emissions, primarily carbon dioxide, is therefore urgently required. At the G8 summit, which took place in Italy in July, 2009, a declaration was made to reduce emissions to limit mean global temperature rise from preindustrial levels to 2 °C. A significant proportion of carbon dioxide emissions comes from power generation from fossil fuels. While nuclear and renewable energy sources could reduce emissions, neither are currently able to meet world energy demand and carbon capture and storage (CCS) is required as the transition is made.

Status of CCS

There are a number of CCS demonstration projects planned, which aim to advance the technologies and prove technical viability at a realistic scale. The high cost of CCS coupled with the technical risks of the developing technology makes investment in such demonstration projects unattractive without government funding or incentives. The EU Emission Trading Scheme (ETS), currently in its second phase, effectively assigns a value to carbon dioxide emissions that will encourage emissions reductions from large point sources, but this and other similar schemes alone are unlikely to bring about wide scale CCS. Governments are now committing funding for demonstration projects to promote the transition to full scale uptake.

Advances in power plant technology can increase overall efficiency significantly. Super critical coal fired boilers can improve the overall net efficiency by over 20%, for example from 38% to 46%,¹ compared to conventional sub critical boilers, reducing carbon dioxide emissions but requiring more capital investment. The UK government is to provide funding for up to four CCS demonstration projects for coal fired power stations each with a capture capability of 300 MW or greater net capacity and has currently budgeted £ 90 million for design and development work for the first project in 2009 - 2010.² Also, the EU, as part of its European Energy Programme for Recovery (EPR), has budgeted € 1.05 billion for CCS to be distributed between seven member states, including

€ 180 million for a 900 MW project by Powerfuel Power Ltd at Hatfield in Yorkshire, UK, which proposes to demonstrate coal gasification with precombustion capture technology and is expected to be completed in 2014. Similar government support is being given for projects worldwide, including Australia, Canada, Europe and the USA.

Because of the large transport infrastructure costs associated with CCS, it has been proposed that 'clusters' are formed linking a number of fossil fired power stations and other industrial sites to a single carbon transportation system.³ Yorkshire and Humber, Teesside, Thames Gateway, the Firth of Forth and Merseyside are all potential locations for multiple CCS projects and cluster development in the UK. The UK government aims to encourage the formation of clusters and the installation of pipelines with capacity to transport captured carbon dioxide from future sources at the earliest opportunity.

Capture technology

There are currently three main routes to carbon dioxide capture: post combustion, precombustion and oxyfuel.

Post combustion capture

Power generation with post combustion carbon capture involves fuel being burned in air with carbon dioxide captured from the resultant flue gas. This method has the advantage that it could be retrofitted to existing plants although the additional plot area and utilities required could make this difficult unless considered in the initial design, hence the emergence of 'capture ready' power plants.

Flue gases tend to be at close to atmospheric pressure with a carbon dioxide concentration of approximately 3% from gas turbines and 10 - 15% from coal fired boilers. The combination of low pressure and low carbon dioxide concentration makes carbon dioxide capture energy intensive, and many developments are focused on lowering this energy penalty. Physical absorption processes, which require a pressure driving force for carbon dioxide removal, do not lend themselves well to this application, primarily because of the large power requirement for flue gas compression. Chemical absorption is better suited, as mass transfer is

driven by chemical reaction. Amine solvents are attracting the most attention as they have already been used for carbon dioxide removal from natural gas on a commercial scale. Primary, secondary, tertiary and hindered amines have different characteristics and have all been applied to carbon dioxide removal from natural gas depending on the gas pressure, contaminant content and outlet specifications. A key consideration given the large volume and low flue gas pressure, is the large absorber diameter required. The primary amine monoethanolamine (MEA) is currently proposed by several licensors because of its fast reaction rate, giving a larger driving force for absorption and lowering the height required for the absorbers. MEA does however degrade through reaction with oxygen, present in flue gases, to form heat stable salts, introducing the need for amine reclaiming and increasing energy requirements.

There is a need to identify a solvent that has a low vapour pressure to minimise losses, is not easily oxidised, is highly reactive and has low heat of reaction with carbon dioxide. Blended amines using a tertiary amine with a primary amine activator show promise while other solvents under development such as chilled ammonia or amino acids have the potential to reduce energy consumption substantially.

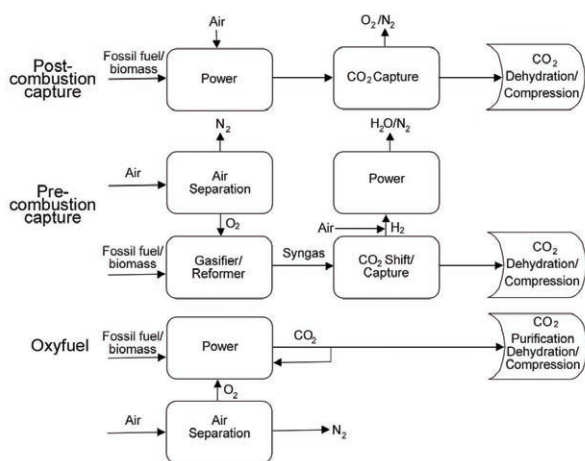


Figure 1. Schematic of carbon capture routes.



Figure 2. Post combustion capture coal fired power plant.



Figure 3. Costain designed cryogenic air separation unit.

Costain has recently been involved in the design of a demonstration project set up to progress CCS. This has included evaluation of new amine solvents and chilled ammonia, which have less susceptibility to degradation by oxygen.

Process schemes are being developed to make the amine absorption process more efficient. Existing technology such as split flow and absorber side stream coolers may be combined with novel ideas such as vapour recompression or multi pressure stripper configurations, to reduce the energy requirements.

Precombustion capture

Power generation with precombustion carbon capture involves production of synthesis gas (H_2 and CO), either from reforming of natural gas or gasification of coal or biomass. The hydrogen yield is maximised by shift reactors operating at successively lower temperatures. The hydrogen is then conditioned and burnt in a combined cycle gas turbine; a process known as integrated gasification combined cycle (IGCC). The advantage of this technology is that the synthesis gas, prior to combustion, is rich in carbon dioxide and at high pressure, making separation of the carbon dioxide less energy intensive and the separation equipment more compact.

Precombustion capture technologies under consideration include both physical and chemical absorption. Chemical absorption techniques, similar to those considered for post combustion capture, could be appropriate for lower carbon dioxide partial pressures. Physical absorption could also be appropriate for precombustion capture and becomes more energy efficient than chemical absorption when the partial pressure of carbon dioxide is high. Physical absorption processes selectively absorb the carbon dioxide in a solvent at high pressure, which is then let down in pressure to liberate the carbon dioxide. The main energy penalty comes from pumping the solvent and either steam stripping or refrigeration depending on the solvent.

IGCC power generation is a relatively new and complex technology. As of 2009, there are five IGCC plants operating worldwide.⁴ Each new plant requires considerable development compared to a plant based on the more mature pulverised coal (PC) technology. IGCC plants do have a potential efficiency advantage over PC plants, one reason being the lower power penalty for carbon capture, but further development on a commercial scale and proven reliability is required before IGCC can become a more widely accepted technology for decarbonised coal fired power.

Developments in precombustion capture include combined reaction/separation techniques to overcome equilibrium limitations in the reactor. Such methods could remove the need for shift reactors and a separate carbon dioxide separation system. One method being investigated is sorption enhanced reforming, where a catalyst and adsorbent packed bed is used to drive the reaction to completion by continual removal of carbon dioxide. High temperature tolerant and hydrogen selective inorganic membranes are also being considered for the reformers with the retentate being mainly carbon dioxide and steam, and the permeate low pressure hydrogen.

Oxyfuel

Oxyfuel combustion of fuels in oxygen rather than air results in flue gas with very high carbon dioxide concentration, typically 75 - 85 mol.% or higher on a dry basis,⁵ compared with 15 mol.% from conventional combustion of coal. The balance of the flue gas is made up mainly of nitrogen, with some oxygen and argon together with SO_x and NO_x impurities. Feed oxygen purity and air ingress are the main factors influencing flue gas composition.

Developments in oxyfuel power generation technology are focused primarily on boiler design for steam turbine power generation, with temperatures maintained at close to conventional levels by recycling of a portion of the carbon dioxide rich flue gas. Adaptation of current boiler

designs to accommodate oxyfuel firing is expected to require relatively small modifications in comparison with oxyfuel gas turbine cycles, which require fundamental design modifications to accommodate the change from a nitrogen rich to a carbon dioxide rich working fluid.

Oxyfuel firing can improve boiler efficiency because of improved overall heat transfer resulting from the higher emissivity of the combustion products and improved heat transfer in the convective section of the boiler.

The main energy penalty arises from the need to produce large quantities of oxygen in an air separation unit. Cryogenic air separation is the most economic option at large scale. It is a very mature technology and only small improvements in performance could be expected, for example through improved compression efficiency. New oxygen production technologies are emerging, which show promise, but are some years from commercialisation at the scale required.

Low temperature separation technology can be applied for purification of the carbon dioxide flue gas to remove oxygen, nitrogen and argon. Temperatures must be maintained above approximately $-55\text{ }^{\circ}\text{C}$, constrained by the triple point and consideration of carbon dioxide solidification, limiting carbon dioxide recovery. Costain developed proprietary hybrid technology, including low temperature distillation and membrane separation, for improved recovery of carbon dioxide. This could potentially be applied to purification of oxyfuel flue gas.

Conditioning and transportation

Large scale transport from source to storage site has been proposed by both pipeline or ship. Carbon dioxide is transported in pipelines at supercritical pressure while shipping of carbon dioxide requires liquefaction, with liquid storage typically at a pressure of approximately 20 bara. As transport distances increase, or volumes transported decrease, shipping becomes more economical than pipeline transport,⁶ and shipping may be competitive at small scale or for remote locations. Pipelines are likely to dominate for larger scale transport especially if common infrastructure can be developed to transport carbon dioxide from major clusters.

Dehydration is required for both pipeline and ship based transport to avoid corrosion of carbon steel pipes and equipment through carbonic acid formation with free water, hydrate formation or erosion. Dehydration specifications vary depending on the type of transport but will require reliable glycol or adsorbent based systems.

Dehydration units based on recirculating triethylene glycol (TEG) may be the best choice for pipeline delivery giving a low capital and operating cost. In Costain's experience of TEG dehydration in natural gas processing, these units can be very reliable and cost effective. Adsorbent based dehydration units using molecular sieve or silica gel is required to dehydrate to the lower levels required for liquefaction. Adsorbent systems are likewise very robust and simple in operation. While dehydration is critical in avoiding corrosion and hydrate formation, it is not a major hurdle in the context of demonstrating feasibility of CCS.

Pipeline transport

To avoid multi phase flow, pipeline transport will be at supercritical pressure in the dense phase, where the carbon dioxide has a density similar to liquid and a compressibility and viscosity similar to gas. Delivery in the dense phase can be achieved by compression or by liquefaction and pumping. The latter has potential to provide energy saving and could be particularly attractive where low temperature cooling water is available or where refrigeration could be generated using an absorption refrigeration system from low level heat through integration with the power plant.

Costain designs large scale compression systems in gas transmission networks. Electric motor drives are typically considered the best available technology from an emissions perspective, although steam turbine drives could also be appropriate where supply of steam can be

integrated with the power plant. The drive type depends on plant turn down and availability requirements; a fixed speed drive may be used to reduce capital cost where production is predicted to be consistent whereas variable speed drives add flexibility for disturbances and turn down.

Although there are a number of carbon dioxide pipelines, particularly in North America, these pipelines generally run through non-populated areas. Carbon dioxide transport for CCS may need to run closer to populated areas, increasing the need to manage safety issues. Carbon dioxide is an asphyxiant, is toxic, and is heavier than air so will tend to accumulate in depressions, potentially for a long time. For this reason pipeline design and routing should account for results of dispersion modelling, including consideration of major failure and release scenarios. Potential leakage points should be kept to a minimum through inherently safe design and the benefits of odorant injection should be evaluated.

An important consideration for carbon dioxide pipeline design is the phase behaviour of carbon dioxide. Inaccuracies in fluid property prediction may come about when trace components are present. As a general trend, increase in contaminant concentrations will increase critical pressure and decrease critical temperature with operation at sufficient pressure to maintain a single phase to avoid surge or pressure drop.

Pipeline corrosion will be prevented by adequate dehydration and monitoring of the dehydration system is crucial. If common pipelines are to be used to transport carbon dioxide from multiple sources then pipeline entry specifications will need to be introduced to limit the variability in fluid properties and avoid free water and potential for corrosion or hydrates.

Valve and vent line design needs to be considered carefully as carbon dioxide will reach low temperatures during venting with the possible formation of 'dry ice' causing plugging and a low temperature safety hazard. Staged depressurisation may be needed to protect carbon steel equipment and pipe work.

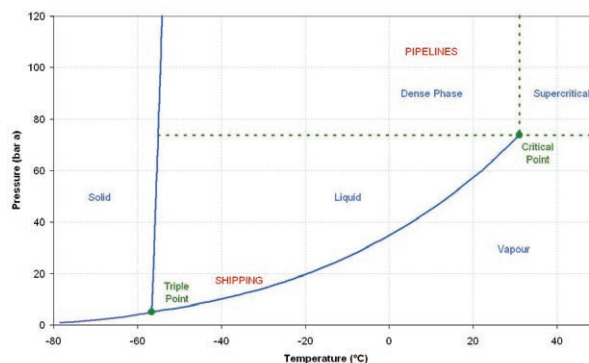


Figure 4. Phase diagram of carbon dioxide.



Figure 5. Costain designed carbon dioxide liquefaction plant for the food industry.

Shipping

Carbon dioxide transport by ship is relatively uncommon, with the current fleet comprising a few small ships transporting food grade carbon dioxide. The design of carbon dioxide carriers is similar to LPG carriers and it is thought that such ships will be built in the same yards.

Transportation by ship requires the carbon dioxide to be compressed, dehydrated and liquefied. Costain has supplied a number of carbon dioxide liquefaction plants for supply to the food industry, including purification to greater than 99.9 mol.%. The compressed and dried carbon dioxide can be condensed against an evaporating refrigerant such as ammonia, prior to passing to storage. Flash and boil off vapour from storage can be recycled to the feed compression system and reliquefied.

An issue to be considered in liquefaction plant design is the build up of inerts, such as nitrogen and oxygen, which will increase compression requirements and may justify a purge system.

Carbon dioxide can exist in the liquid phase above its triple point pressure of 5.3 bara, and is typically stored at up to approximately 20 bara. As the carbon dioxide liquefaction and storage capacities needed for CCS are considerably higher than those conventionally used for industrial supply, this storage pressure could be challenged. Higher storage pressures require less refrigeration power but greater investment in thicker walled storage vessels, and may be optimal in some applications.

Onshore storage must provide adequate volume for shipping logistics, the size and number of carbon dioxide tankers, the distance to the storage location, time taken to fill, discharge and any allowances for shipping delays. The capital cost of both the onshore storage and ships is very significant and will be an important factor when selecting design parameters.

Parallels can be drawn between shipping for CCS and the long established liquefied natural gas (LNG) chain, in which there is considerable experience in liquefaction, shipping and in some cases floating facilities for regasification. Floating LNG is an area where Costain has developed considerable capability for engineering and design of process topside equipment at significantly larger capacities than being considered for carbon dioxide transport.

Geological storage

There is potential to store carbon dioxide in geological formations such as depleted oil or gas fields, deep saline formations or unmineable coal seams. Carbon dioxide has been injected into geological formations in Norway, USA and Algeria demonstrating that such storage is feasible. The Intergovernmental Panel on Climate Change (IPCC) estimates that geological storage has the potential of storing up to 99% of the injected carbon dioxide for a thousand years.⁶ Depleted oil and gas reservoirs may be attractive, and have been extensively modelled so there is a good understanding of how they behave, specifically their storage capacity and leak potential. Also, depleted oil and gas fields have the advantage of having infrastructure in place that may be utilised for carbon dioxide storage if the changeover from gas to carbon dioxide is timed correctly. Some enhanced oil recovery projects expect to store at least part of the injected carbon dioxide. Deep saline formations offer significant storage potential many times that available in oil and gas fields and they are located close to emitters, including the North Sea, Europe and the Texas Gulf Coast. Unmineable coal seams can offer the opportunity for natural gas recovery as the carbon dioxide displaces the natural gas but the mechanisms that control this are not well understood and this method of storage is still under evaluation.

Ocean storage

Storage of carbon dioxide deep in the sea has also attracted some interest, through creation of carbon dioxide lakes or through dissolution. Neither of these two options is likely in the near term until the environmental implications are understood, as lowering of the pH through

formation of carbonic acid could harm marine life. Also, the permanency of sequestration is less certain, with predictions that the carbon dioxide could be released back into the atmosphere over hundreds of years. In fact, the London Protocol and OSPAR Convention currently prohibit this form of storage in the North East Atlantic.

Mineral storage

The potential for mineral carbon dioxide storage is being investigated, where carbon dioxide would be reacted with metal oxide bearing materials to form a solid product, providing the potential for long term storage and low risk of future release. However, the reaction kinetics of such carbonation is very slow and requires energy intensive preparation of the metal oxides to facilitate the reaction. This technique may overcome barriers that exist with geological storage in certain regions but the technology in its current state has a prohibitive energy penalty when compared to geological storage.

Conclusions

A number of CCS projects are planned to demonstrate the scale up of the technologies in the transition prior to adoption at a commercial scale. This is largely dependant on government support and funding. Once proven, an appropriate financial and regulatory framework would be needed if CCS technologies are to be more widely implemented by 2020.

Capture technology choice is dependent on application. Advances are being made in all three main capture techniques and it is too early to say which will be most widely adopted.

It would be expected in the long term that pipeline transportation will be favoured, particularly if CCS clusters can be formed. For demonstration projects and smaller or more remote sources, liquefaction and shipping could be appropriate. A common transport infrastructure could make CCS more attractive by allowing industry to share the cost.

Geological storage in depleted oil and gas reservoirs or saline formations currently appears to offer the best solution for long term storage. Depleted oil and gas fields may be convenient for early projects and a number of sites have been identified. There is significantly greater storage potential in deep saline formations and in the long term these will be required to meet global storage needs. [13](#)

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Figure 6. The Flex LNG Producer (permission to publish granted by Flex LNG and Samsung Heavy Industries).