CARBON CAPTURE AND STORAGE/UTILISATION TECHNOLOGY PRIMER: A SUMMARY

BACKGROUND

Carbon capture refers to the process of separating CO_2 from power plants and other industrial sources of emissions. The CO_2 is then sequestered (i.e. held in long-term isolation) to prevent the CO_2 from reaching the atmosphere and contributing to climate change.

Carbon Capture and Storage (CCS) is widely regarded as an important technology to mitigate climate change. The International Panel on Climate Change (IPCC)[1] assesses that CCS has the potential to reduce overall mitigation costs and increase flexibility in achieving greenhouse gas (GHG) emission reductions. Simulations such as MiniCAM[2] in *Figure 1* show that CCS is an important component of a lowest-cost portfolio of measures to mitigate global GHG emissions. The International Energy Agency (IEA) also assesses that CCS is a key technology to achieve its BLUE Map[3] emissions reduction scenario, without which overall costs to reduce global emissions would increase by 70%.

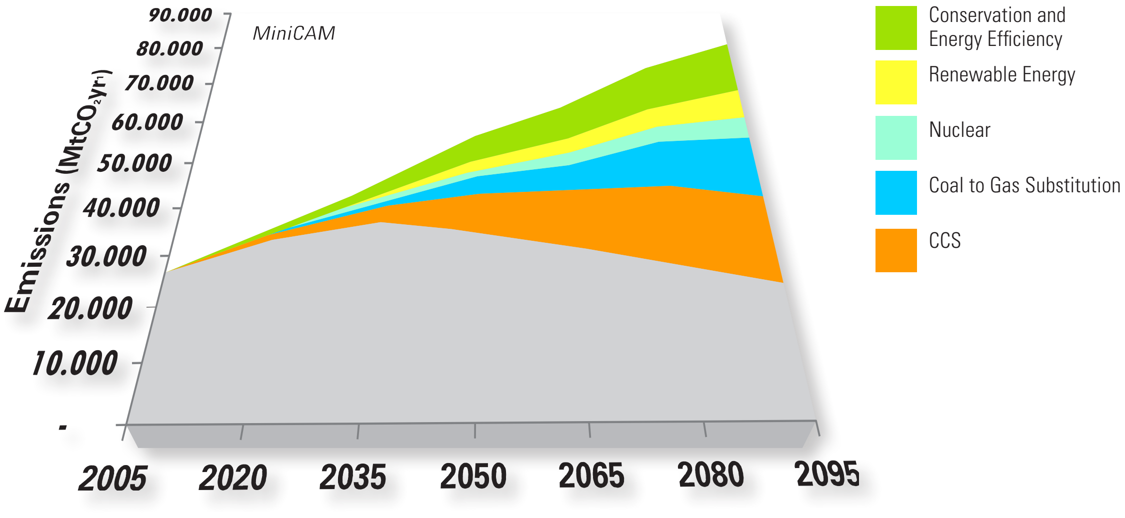

Figure 1: Integrated assessment model (MiniCAM) for global CO_2 emissions[2]

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[1] Intergovernmental Panel on Climate Change (IPCC) Special Report on Carbon Dioxide Capture and Storage (2005). http://ipcc.ch/pdf/special-reports/srccs/srccs_wholereport.pdf

[2] The Mini Climate Assessment Model (MiniCAM) is an integrated assessment model considered by IPCC to estimate global GHG emissions. The results are elaborated in the IPCC 4th Assessment Report (AR4).

[3] The IEA BLUE Map scenario assumes that global emissions is reduced to half of 2005 levels by 2050. The scenario is published in IEA's Energy Technology Perspectives 2008.

POTENTIAL APPLICATION IN SINGAPORE

Singapore is a small island state with limited access to renewable energy sources due to its physical size and geographical conditions. 97% of the energy demand in Singapore is met through the use of fossil fuels. Singapore has taken significant steps to address its energy demand through various energy efficiency and conservation initiatives. In addition, Singapore has invested significantly in clean energy technologies such as solar to maximise its capacity to harness renewable energy. Despite these efforts, fossil fuels are expected to remain the dominant source of energy for Singapore in the foreseeable future.

Singapore's GHG emission in 2005 was about 40 million tonnes of CO_2.[4] Power generation, together with energy-intensive industries such as the refinery, petrochemical and semiconductor cluster's, account for the bulk of Singapore's emission. These are potential areas for the application of CCS technology locally.

Singapore is committed to mitigate carbon emissions as part of a global effort to address climate change. The government has submitted a pledge to the United Nations Framework Convention on Climate Change (UNFCCC) to reduce GHG emissions by 16% below business-as-usual levels in 2020, contingent on a legally binding global agreement in which all countries implement their commitments in good faith. Climate change is a long-term challenge. In mitigating climate change, the Cancun Agreements call for all Parties to cooperate in achieving peak global and national GHG emissions as soon as possible. Beyond 2020, Singapore would need new solutions to develop on a low emissions pathway while sustaining economic growth. ***Given that Singapore has limited access to alternative energy, the authors assess that CCS is a key technology for Singapore to continue to use fossil fuel resources in a cost-effective manner while meeting its long-term GHG mitigation obligations. In the context of Singapore, CCS solutions are likely to take the form of carbon capture and storage/utilisation (CCS/U).***

CCS/U is expected to bring the following benefits to Singapore:
(a) Significantly lowering carbon emissions from industry and power generation.
(b) Enabling a wider range of sources for baseload generation, to diversify Singapore's fuel mix for enhanced energy security.
(c) Generating economic returns from a potential new industry for sustainable green products from carbon.

CARBON CAPTURE TECHNOLOGIES

Technologies for CO_2 capture can be broadly classified into three categories. These are (i) post-combustion capture, (ii) pre-combustion capture and (iii) oxyfuel combustion *(see Figure 2)*. Since capture from industrial processes employs more or less the same technologies, it is not discussed separately.

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[4] Singapore National Climate Change Strategy (2008), National Climate Change Committee. http://app.mewr.gov.sg/data/ImgUpd/NCCS_Full_Version.pdf

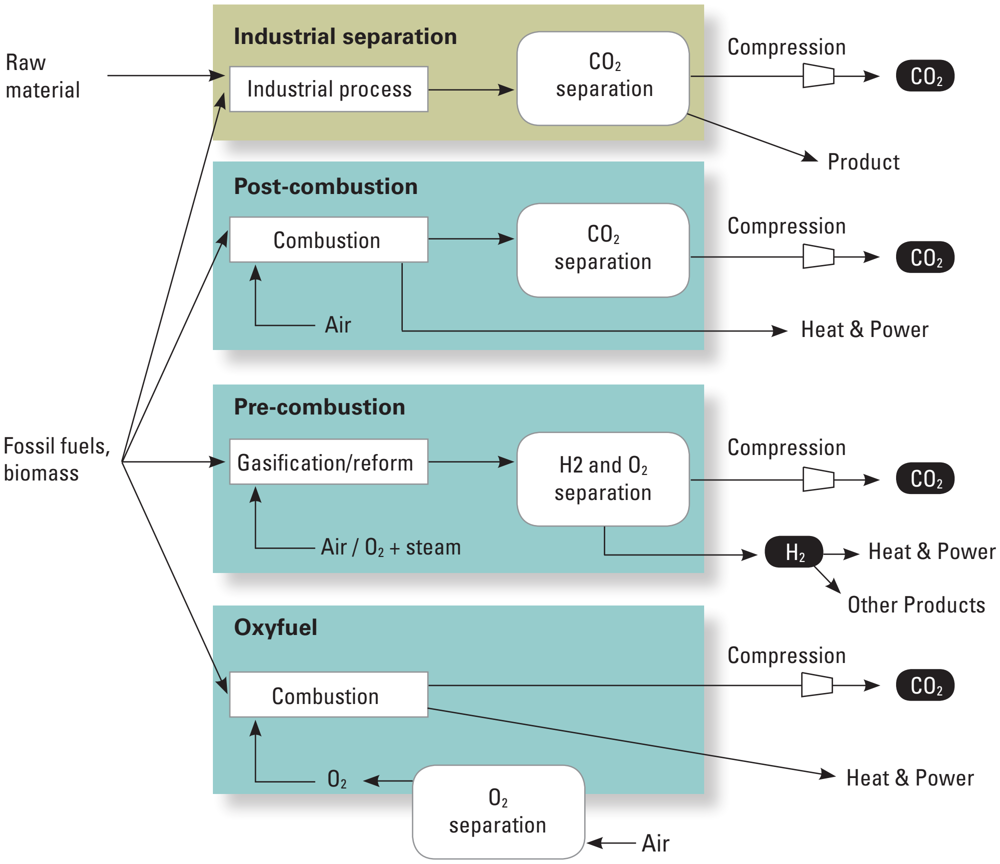

Figure 2: Types of carbon capture scenarios[5]

Post-combustion Capture

The combustion of fossil fuels produces an exhaust stream of flue gas. Post-combustion capture refers to the separation of CO_2 from other gases and impurities in this gas mixture. The process is challenging for several reasons. First, the concentration of CO_2 in a flue gas mixture is rather low and separating it from non-condensable gases (e.g. nitrogen) is complex. Second, the flue gas exists at a relatively low pressure. The volume of gas that has to be treated is thus high. Third, the capture process consumes a significant amount of energy. This requirement is referred to as energy penalty, which is defined as the proportion of energy produced by a power plant that is diverted to power the capture process. The energy penalty has to be kept to a minimum to reduce operating cost.

The main technologies for post-combustion capture are as follows:

(a) **Solvent absorption** makes use of a liquid solvent (typically an amine) to absorb CO_2 that is contained in the flue gas mixture. The dissolved CO_2 is subsequently removed from the solvent using steam. Although the process of absorbing CO_2 requires minimal energy input, the process of regenerating dissolved CO_2 is

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[5] Adapted from Figure TS.3 of the Intergovernmental Panel on Climate Change (IPCC) Special Report on Carbon Dioxide Capture and Storage (2005). http://ipcc.ch/pdf/special-reports/srccs/srccs_wholereport.pdf.

energy intensive. Solvent absorption is an established technology and is being used to manufacture hydrogen, ammonia and methanol. Studies indicate that the cost of CO_2 capture for a 500 MW pulverised coal power plant with absorption technology is about US$49.7/tonne of CO_2, and the energy penalty is about 32%.

(b) **Solid adsorption** involves the use of a solid mass-separating material known as an adsorbent. There are two physical properties that enable a material to serve as an adsorbent. The first relies on the affinity of CO_2 towards the adsorbent to extract CO_2 in a technique known as equilibrium separation. The second exploits the differences in the rate of diffusion of various substances into the adsorbent to achieve kinetic separation. In a typical separation process, an adsorbent is put through three possible operation cycles to capture CO_2. These are pressure swing adsorption (PSA), vacuum swing adsorption (VSA) and thermal swing adsorption (TSA). VSA cycle is more attractive than a PSA cycle because the latter requires compression of large volumes of gas. TSA cycle can be a promising alternative if waste heat is available in a plant. Solid adsorption separation is a mature technology in processes such as air-separation and hydrogen purification. However, its application in the area of CO_2 capture from flue gases mixture is a rather recent development. Recent studies indicate the high potential of solid adsorption technology for CO_2 capture. The initial costs estimates are promising. At present, a few pilot-scale demonstrations (including one in Singapore[6]) are investigating the effectiveness of the VSA process that employs equilibrium separation for the capture of CO_2. The commonly used adsorbents in these studies are zeolites and carbons as these are non-exotic materials and are fairly inexpensive for large-scale deployment.

(c) **Membranes:** A membrane is a barrier, which allows for the selective permeation of one component of a fluid mixture from one side to another, i.e. from the feed to the product. The mechanism of separation can be based on (i) the solubility of a gas in the membrane material, (ii) the molecular size, in the case of molecular sieving, or (iii) differences in adsorption properties. Membranes can be made of polymers, carbon, and inorganic materials such as zeolites, etc. The membranes can be fabricated as sheets or hollow fibers. Several membrane processes are being explored for post-combustion CO_2 capture, including simple membrane processes, hybrids with others, etc. One main challenge in using membrane technology arises from the fact that large surface areas are required for the separation, owing to the large quantities of relatively low concentration CO_2 that has to be concentrated. Furthermore, there is no known membrane separation unit operating at commercial scales in order to obtain estimates of reliability and costs. A mature technology in other fields, membranes still need to be explored in detail, to adapt for efficient use in post-combustion CO_2 capture processes.

The advantage of post-combustion capture is that it requires little modification to existing equipment and process configuration, as it is applied to the tail-end of a combustion process. Post-combustion capture is the only capture technique that can be practically applied to existing equipment through retrofits. *The authors assess that post-combustion capture is an important technology given that it has the greatest potential application in the short term. In the longer term, post-combustion capture will continue to be relevant for industry application, especially where it is not feasible to redesign entire industrial processes to facilitate carbon capture.*

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[6] A pilot plant study commissioned in Singapore to investigate VSA process for CO_2 capture from power plant flue gas is now underway. This is a collaboration project among the adsorption and process systems research groups at NUS, NTU and ICES.

Pre-combustion Capture

Pre-combustion capture refers to the conversion of fuel into hydrogen where the carbon content of the fuel is stripped out as CO_2 in the process. A pre-combustion capture process typically comprises of three stages. The first stage involves the conversion of a primary fuel source such as coal, oil, biomass and natural gas into syngas (a mixture of CO and H_2). This is achieved by reacting the primary fuel with steam (known as 'steam reforming') or oxygen (known as 'partial oxidation' or 'gasification'). In the second stage, the syngas is treated to convert CO to CO_2 and H_2 by reacting it with steam. This reaction is known as the Water Gas Shift (WGS) reaction. Finally, the CO_2 is separated from the CO_2/H_2 mixture using adsorption techniques (similar to those used for post-combustion capture) to produce a CO_2 stream. The remaining H_2 is used as a fuel or for chemical production. A schematic representation of the pre-combustion capture process is shown in *Figure 3*.

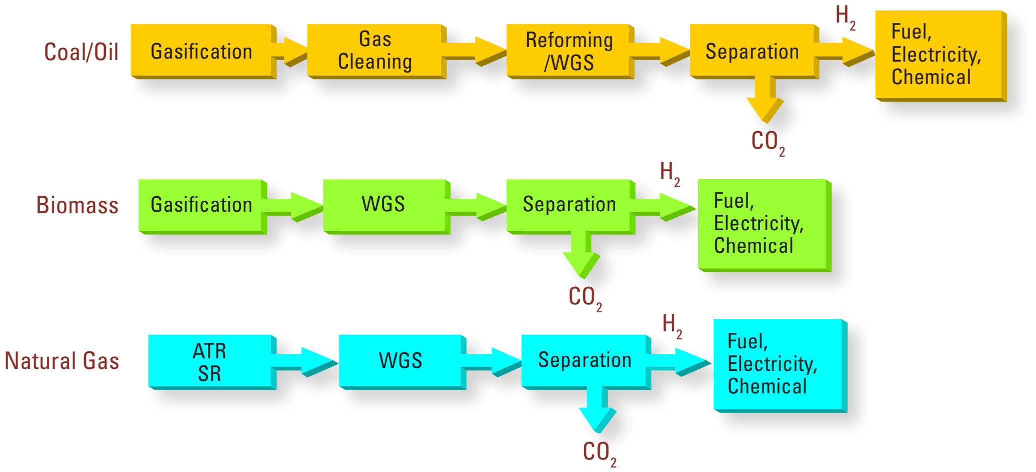

Figure 3: Pre-combustion capture process for various fuel types

Current pre-combustion systems typically make use of physical or chemical solvents for CO_2 separation. These processes are expected to remain the predominant technique for CO_2 separation in the near term. However, they are not widely applied as they are energy-intensive and involve multiple steps. They are also expected to be less relevant in future with the emergence of new pre-combustion capture technologies with higher performance and lower cost.

Intense R&D efforts are underway worldwide to develop new pre-combustion capture technologies. Majority of the research in this area is focused on Sorption Enhanced Hydrogen Production (SEHP), which combines the various reaction steps such as steam reforming, WGS, and CO_2 separation in a single reaction to enhance efficiency. Some of these technologies are discussed below.

(a) **Membrane separation.** Membrane reactors are an attractive option for CO_2 capture in gas-fired power stations because they combine the efficient conversion of natural gas to H_2 for power production with the separation of CO_2 in a single reactor. Current research is focused on developing membranes with high selectivity, long-term hydrothermal stability, overall durability and sulphur tolerance.

(b) **Carbonation of CaO.** This technology integrates the WGS reaction with in-situ CO_2 capture using CaO as a sorbent. The used sorbent is heated to release the CO_2 and regenerate CaO for reuse in the process. A number of pre-combustion systems makes use of CaO as a sorbent given its high CO_2 affinity and the availability of low cost CaO-based materials. This reaction route is also attractive because of its efficiency in capturing CO_2.

Pre-combustion capture offers several advantages, namely:

i. Proven industrial scale technology in oil refineries, ammonia and urea manufacturers.
ii. Capable of capturing 90–95% of CO_2 emissions.
iii. Wide application to all primary fuels types regardless of their physical state (i.e. solid, liquid or gas).
iv. Lower CO_2 capture costs compared to post-combustion capture and oxy-fuel technologies due to its lower energy penalties and higher energy efficiencies.
v. Capable of producing a mix of electricity and hydrogen (for use as a fuel or chemical feedstock) on a large scale and at high levels of thermal efficiency.

The authors assess that pre-combustion capture can improve the performance and lower the cost of CO_2 capture in the longer term. There is significant scope for innovation to optimise the various processes in pre-combustion capture.

Oxy-fuel Combustion

Oxy-fuel combustion refers to the technology where fossil fuels are burnt in almost pure oxygen instead of air. The utilisation of this approach overcomes the most serious drawback of post-combustion capture processes, which is the difficulty of separating CO_2 from a flue gas mixture containing N_2 (nitrogen). Since N_2 is removed prior to combustion, the flue gas mixture leaving a combustion chamber consists of only CO_2, H_2O (water), NO_x (nitrogen oxides) and SO_x (sulphur oxides). After taking the necessary heat recovery steps, the flue gas mixture is cleaned up to remove NOx and SO_x. A further compression step separates the CO_2 and H_2O to produce a relatively pure CO_2 stream that is ready for sequestration.

The key difference between a post-combustion and an oxyfuel combustion process lies in the latter's need for an air separation unit (ASU) to produce a stream of 95–99% pure oxygen. This implies additional capital costs and land requirements for retrofits. However, several studies suggest that there are various economic advantages of retrofitting a post-combustion capture plant with an oxy-fuel combustion plant. There is significant potential to develop more energy efficient air separation processes that will further advance the oxy-fuel combustion technology. *The authors assess that oxy-fuel has the potential to bring about a significant improvement in CO_2 capture efficiency. However, several challenges such as producing oxygen economically and technologies (materials, processes, etc.) that would allow combustion with oxygen have to be resolved. Furthermore, large scale demonstrations of this technology are still at a preliminary stage.*

Chemical looping combustion (CLC) is a variant of oxy-fuel combustion that can potentially improve the performance of carbon capture significantly. This technology uses two separate reactors (an air reactor and a fuel reactor) together with an oxygen carrier to form a combustion system. The process starts in the air reactor where the oxygen carrier absorbs oxygen from air. The oxygen carrier is then transferred to the fuel reactor where it releases the oxygen for combustion with a fuel. CLC process results in two separate flue-gas streams. The stream leaving the air reactor contains N_2 and some remaining O_2, while the stream leaving the fuel reactor contains mainly CO_2 and steam. An almost pure stream of CO_2 is obtained by condensing the steam. The efficiency of the CLC process is largely dependent on the performance of the oxygen carrier. The carrier must also be able to support efficient fuel combustion. Transition metal oxides such as nickel, copper, cobalt, iron and manganese are good choices. Recently, non-metal oxides such as calcium sulphate and strontium sulphate have also been found to be good oxygen carriers. ***The challenge in realising this technology is to find a good oxygen carrier that is inexpensive, available in large quantities, has sufficient oxygen capacity and is able to withstand large numbers of reduction/oxidation cycles and mechanical handling without loss in performance.*** In addition, there are challenges in moving large amounts of solids at scales that are significantly larger than the current technologies (e.g. fluidised bed).

CARBON STORAGE

In the long-term, Singapore needs access to some form of carbon storage in order for carbon capture and sequestration to scale up emissions reductions. There are three broad categories of carbon storage options, namely:

i. Geological storage – this involves storing captured CO_2 in geological formations, e.g. rocks, aquifers etc. through different trapping mechanisms. Depleted oil fields are potential sites for long-term CO_2 storage as they possess the necessary geological formations. Enhanced Oil Recovery (EOR), a technology in which CO_2 is injected into producing wells to enhance productivity, can be an economically viable option for CO_2 storage. Studies are underway at various sites to assess the long-term impacts.
ii. Biological storage – this exploits the natural process through which biomass accumulates CO_2 directly from the atmosphere, for example, biofixation of CO_2 by microalgae and other forms of vegetation.
iii. Ocean storage – this method involves the direct dissolution of captured CO_2 into the ocean or injecting captured CO_2 into deep water (i.e. more than 1 km deep).
iv. Mineralisation – this method refers to the reaction of CO_2 with naturally occurring minerals to form carbonates.

It is worth pointing out that Singapore does not have significant sites that can support geological and ocean storage. Hence, the authors assess that mineralisation offers the maximum potential for CO_2 storage and will be elaborated here.

Mineralisation

Mineralisation refers to the process of reacting CO_2 with minerals (specifically silicates) to form solids such as magnesium carbonate and silica. The stable nature of these products ensures that leakage of CO_2 is negligible. Minerals that can be used to react with CO_2 are abundant. For example, the quantity of magnesium silicate rock found in the Earth's crust far exceeds the amount that is needed to mineralise all the CO_2 produced from the combustion of global fossil fuel reserves.

CO_2 mineralisation occurs naturally on geological time scales (i.e. millions of years). This process can be accelerated through the use of carbonation reactors. e.g. The US National Energy Technology Laboratory (NETL) has developed a state-of-the-art reactor that enables CO_2 mineralisation to take place over a time span of hours. This technology involves reacting CO_2 with silicate minerals, in particular, finely-grounded olivine or heat-activated serpentine that is suspended in a chemical solution under high pressure and high temperature conditions.

In the last decade, a lot of R&D efforts have focused on developing methods for extracting magnesium or calcium from minerals or industrial by-products and wastes using strong or weak acids, alkali solutions and ligands. These methods can potentially lower the energy needs for crushing and grinding silicate minerals. However, using chemicals that cannot be completely recovered or re-used would increase processing costs.

CARBON UTILISATION

After CO_2 is captured, it has to be sequestered to prevent the CO_2 from reaching the atmosphere and contributing to climate change. Carbon utilisation refers to the use of CO_2 as a raw material to produce useful materials. This is an attractive option to sequester CO_2 because the value of the products created improves the overall economics of the entire carbon capture and sequestration process. A wide range of potential products can be derived from CO_2. However, the challenge is that CO_2 is a stable compound and thus it is potentially energy-intensive to get CO_2 to react with other substances. It is important that any utilisation option should be net CO_2-negative or neutral, i.e. the energy required for the utilisation should come from a source that emits less CO_2 than what is being converted in the utilisation process. Furthermore, the product of this utilisation must not release the CO_2 back into the atmosphere during its lifecycle. As such, few CO_2 derived products have been commercialised or produced in a large scale with the sole motive of CO_2 utilisation. Figure 4 shows the potential products of CO_2 divided into four major groups.

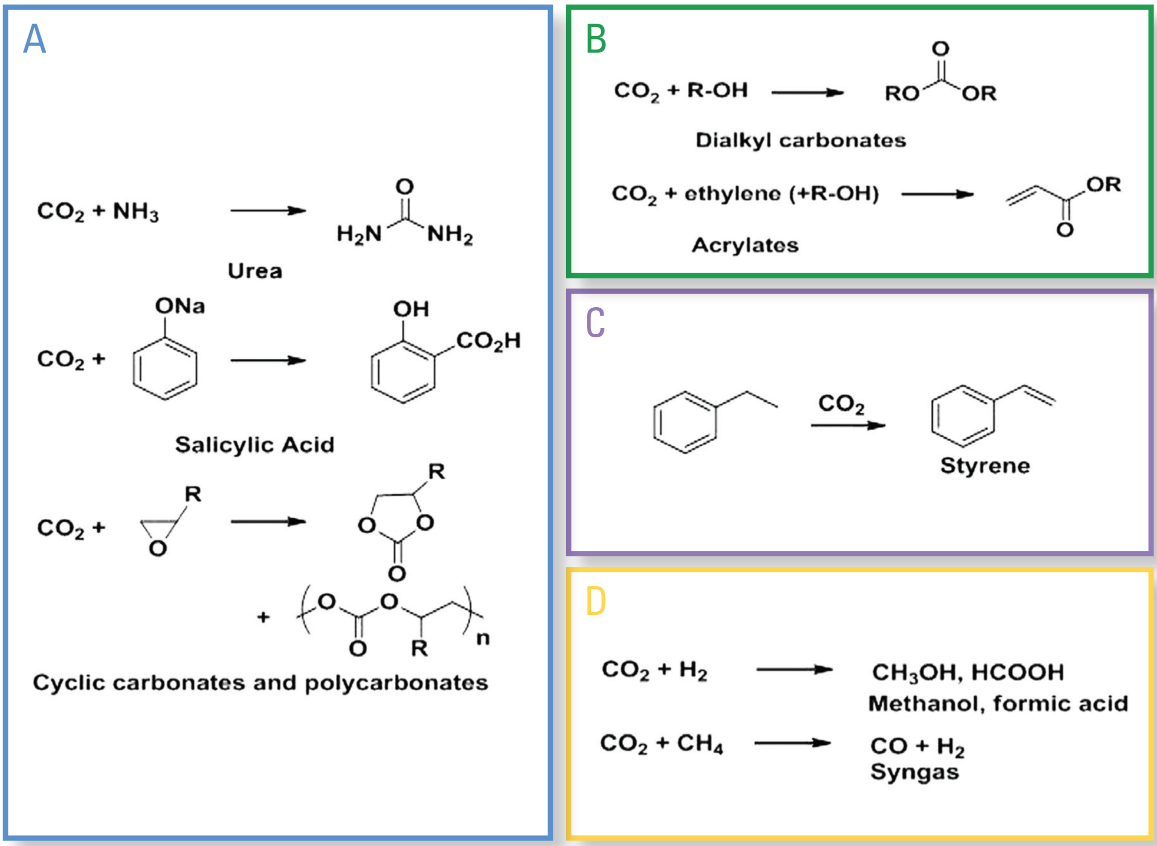

Figure 4: Four major groups of potential CO_2 products obtained from chemical manufacturing

Group A

Group A comprises of products that are already produced from CO_2 at commercial scale, and for which efficient carbon utilisation technologies are available. Currently, there is only one major industrial process that utilises CO_2 for producing chemicals in large quantities (i.e. the production of urea from CO_2 and ammonia, for use as fertilisers). Globally, more than 100 Mt of CO_2 are consumed for this process. This represents about 99% of all CO_2 converted in the chemical industry, but makes up for less than 1% of the global anthropogenic CO_2 emissions. The production of salicylic acid, cyclic carbonates and polycarbonates each consumes lower amounts of CO_2 (i.e. less than 0.1 Mt of CO_2 emissions/year) compared to the production of urea. However, it is worth noting that that the CO_2 consumed in this form is eventually released into the atmosphere and hence does not strictly qualify as a CO_2 reduction option, if viewed in the global context. Aliphatic polycarbonates have been commercialised on the small scale for specialty applications in barrier coatings and automotive parts. A potentially larger market for these polycarbonates is in the manufacture of polyurethane foams.

Group B

This group consists of chemicals that utilise the entire CO_2 molecule, but the technologies to do so efficiently are not available yet. Examples of products in this group include diphenyl carbonate to make polycarbonates for water bottles and laptop casings, as well as acrylic acid or acrylates to make polyacrylates for adhesives, dispersants for paint, and as a fire retardant.

Group C

CO_2 is used in this group to produce styrene, which is then used to produce polystyrene for various items such as rubber, plastic, fibreglass, food containers and automobile parts.

Group D

This group is made up of chemical products derived from hydrogenation or reforming of CO_2. An example is methanol, which can be used as a transportation fuel. However, the feasibility of this technology depends on the availability of renewable source of hydrogen.

The authors assess that, owing to major mismatches in scale, CO_2 utilisation will become an attractive option for Singapore, if significant advances in technologies, or global markets for CO_2 derived products become a reality. In particular, the authors recommend that Singapore can explore potential synergies within its refining and petrochemical industry to exploit opportunities for carbon utilisation from concentrated CO_2 streams that already exist in Jurong Island.

CCS/U IN SINGAPORE

Considerable research is underway in Singapore on various aspects of CCS/U. Most notably, the A*STAR Thematic Strategic Research Program (TSRP) on CCU has seven current projects, four on various types of carbon capture and three on storage /utilisation.

The four capture projects involve adsorption-based post-combustion capture, membrane-based pre-combustion capture, oxy-fuel combustion via chemical looping, and sorption-enhanced water gas shift reaction. Except the first project, which has built a pilot plant at the Institute of Chemical and Engineering Sciences (ICES) to capture at least 200 kg/day of CO_2, the others are still at the laboratory scale. While the work shows promisingly low energy penalties for carbon capture, significant scale-up issues need to be addressed and test-bedding work at pilot and/or industrial scales (approximately 10-1000 tonnes of CO_2/day) is required to demonstrate success and for eventual commercialisation.

The three CCU projects on storage/utilisation involve mineralisation for landfill applications while producing building materials (e.g. sand, cement) as by-products, direct reforming of CO_2 using methane to produce syngas and hydrogen, and fixation of CO_2 in microalgae to produce biodiesel. All these projects are at the laboratory scale and require further work and support to demonstrate success at larger scales.

In addition to the above TRSP CCU projects, other CCS/U work is in progress in the universities and research institutes of Singapore. These include carbon capture/storage via gas hydrate technology, conversion of CO_2 to hydrocarbons in a Fischer-Tropsch-like process, mineralisation of CO_2 to produce carbonate nanoparticles, converting CO_2 to useful products with the help of solar or electrical energy, and other ways to produce useful fuels, intermediates, chemicals, fuels, and final products. However, all of these technologies are highly nascent and require much further work and support.

There is a need to support and capitalise on these ongoing efforts by investing now in fundamental and test-bedding R&D on materials, processes, and systems to develop CCU technologies that cater to both local and global markets in the long-term (2025 and beyond).

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Acknowledgement

The authors have benefited from comments from several colleagues from NUS, NTU and ICES as well as from the following governmental agencies: A*STAR, EDB, EMA, NCCS and NRF. We would also like to thank Karthik RAMADOSS (NUS) for his extensive and meticulous efforts in gathering data and information from various sources. Finally we thank Ms Khai Lin Anne QUAH (Tropical Marine Science Institute) for her tireless effort in updating and consolidating the many versions of this Technology Primer. The authors also convey their condolences to the family of Dr Rong YAN, a former lead author of this Primer, who has passed away.

This report was first published in August 2011. The contents of the primer reflect the views of the authors and not the official views of the government agencies. The publication of the primers has been made possible by NCCS and NRF, and reproduction of the content is subject to the written consent of the authors, NCCS and NRF.