

# CARBON CAPTURE & STORAGE/UTILISATION Singapore Perspectives



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# EXECUTIVE SUMMARY

## General

- Carbon capture and storage/utilisation (CCS/U) from major stationary sources is a potential technology which can help reduce carbon emissions. However, challenges such as achieving cost-effectiveness and low energy penalties for CCS/U and finding demand for carbon utilisation products need to be overcome.
- While CCS implementation is a nearer-term option due to its greater technological maturity, the lack of suitable storage sites in Singapore may require us to look at CO<sub>2</sub> utilisation instead.
- The traditional material-centric R&D approach alone will be unable to address the CCS/U challenges. Integration of materials, process, and system considerations coupled with productive interactions across traditional disciplines will be critical.
- The material and technology research needs related to CCS/U must be evaluated based on their performance in the context of the overall process/system. This overall system-level process performance includes economic viability (CAPEX and OPEX), use of green feedstocks, improved catalysts to accelerate the kinetics of CO<sub>2</sub> transformation into fuels and chemicals, and the minimisation of energy penalty and plant footprints. Hence, this holistic process and systems approach should constitute the basis for all future R&D proposals in CCS/U.

## Carbon Capture and Concentration

- Approximately 84% of Singapore's CO<sub>2</sub> emissions are from stationary sources, with the majority of these emissions at 3% CO<sub>2</sub> concentration due to Singapore's usage of natural gas for power generation.
- As a result of the low CO<sub>2</sub> concentration in emission streams, Singapore's challenge lies in lowering the energy penalty for capturing dilute CO<sub>2</sub> streams.
- Among the three options for CO<sub>2</sub> capture from stationary sources, namely pre-, oxy- and post-combustion, pre-combustion technology based on natural gas offers the lowest energy penalty. Thus, pre-combustion is preferable from an energy penalty perspective for future power plant developments. However, post-combustion and oxy-combustion may be easier to retrofit for existing power generation plants.
- While there is a range of technological options for carbon capture being heavily researched internationally, a clear winner is not yet imminent.
- In the near term, it is recommended that new absorption solvents, adsorption media and processes, and innovative membranes be explored.

## **Carbon Capture & Storage/Sequestration**

- The absence of suitable storage sites in Singapore means foreign sites will have to be sought. International geopolitical and corporate negotiations will be necessary if Singapore decides to pursue CCS. Furthermore, R&D for the long-range cost-effective transport of concentrated CO<sub>2</sub> to off-shore or regional sites will be essential.

## **Carbon Capture & Utilisation**

- The geological and geopolitical constraints limiting CO<sub>2</sub> storage similarly limits use of CO<sub>2</sub> for Enhanced Oil Recovery (EOR) and Enhanced Coal Bed Methane Recovery (ECBMR). Other utilisation options such as innovative reactions to convert CO<sub>2</sub> into useful products via physical, chemical, or biological pathways become more relevant. However, cost estimates must be refined further through detailed modelling of the various chemical routes through the unit operations.
- Since CO<sub>2</sub> is a highly stable molecule, its conversion will require additional (preferably renewable) energy inputs, novel catalysts and processes, and/or high-energy reactants. One example is hydrogen, which is a crucial reactant for CO<sub>2</sub> utilisation. It can be obtained via electrolysis of water or from gasification of fossil fuels. Due to Singapore's constraints in renewable energy generation, careful assessment on the best way to utilise the renewable energy (whether direct use of electricity or utilising for H<sub>2</sub> production and CCU) may be required.
- For CCU to be practical, there must be a demand for the products. However, utilisation of Singapore's CO<sub>2</sub> alone to produce chemicals such as formic acid, acetic acid and formaldehyde would far surpass the global demand for these products. The only global markets of scale comparable to Singapore's CO<sub>2</sub> emissions are liquid fuels, such as methanol, ethanol and other hydrocarbons, and mineralisation products for the building and construction industry.
- CO<sub>2</sub> utilisation via biological means such as micro-algae is limited by the lack of availability of resources in Singapore, such as land and water. Due to the low mitigation potential of micro-algal utilisation compared to the land area required, utilising the land for other resources such as solar PV would be more beneficial in terms of CO<sub>2</sub> abatement. However, despite the minimal impact on mitigation, they may offer some niche and attractive options for CO<sub>2</sub> utilisation from an economic perspective such as the production of nutraceuticals and pharmaceuticals.

# 1. INTRODUCTION

Carbon capture and storage/utilisation (CCS/U) reduces emissions by capturing and either storing the CO<sub>2</sub> in storage sites or converting the captured CO<sub>2</sub> into usable products, thus preventing it from being emitted into the atmosphere. As long as our reliance on fossil fuels remains, CCS/U has potential to be an important part of our strategy to reduce CO<sub>2</sub> emissions.

Several countries and international/national groups and agencies such as the Intergovernmental Panel on Climate Change (IPCC), the International Energy Agency (IEA), the US Department of Energy (US DOE), the US Environment and Protection Agency (US EPA), academia, consultancies, and non-profit organisations have issued CCS/U roadmaps and publications. These highlight the importance of CCS/U in reducing long term emissions to avoid the most severe impacts of climate change<sup>1</sup>. This CCS/U Technology Roadmap builds upon previous studies, but is tailored to Singapore's CO<sub>2</sub> emission-profile and geological circumstances.

## 1.1 GOAL AND OBJECTIVES

The goal of developing this roadmap is to help identify the requirements needed to accelerate research, development, demonstration and deployment of CCS/U in Singapore should Singapore decide to deploy CCS/U in the future.

The objectives of this roadmap are to:

1. Present a literature review of the global state of CCS/U today;
2. Categorise Singapore's emissions according to the concentration of CO<sub>2</sub> in the emission streams;
3. Identify and study various Singapore-relevant options for CCS/U;
4. Quantify the potentials of various CCS/U technologies in terms of CO<sub>2</sub> reductions; and
5. Identify R&D strategies that would accelerate the deployment of CCS/U in Singapore in the longer term.

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<sup>1</sup> To prevent the most severe impacts of climate change, the Intergovernmental Panel for Climate Change's 5<sup>th</sup> Annual Report (AR5) concluded that there is a need to limit emissions from human activities to limit global warming to a maximum temperature rise of 2°C above pre-industrial levels.

## 2. SINGAPORE'S CO<sub>2</sub> EMISSION BASELINE & CONCENTRATION PROFILE

The cost incurred for CCS/U depends significantly on the concentration of CO<sub>2</sub> in the flue gas/process stream, and this will be described and discussed in further detail in subsequent sections. Capture from streams with lower CO<sub>2</sub> concentration from dispersed sources (e.g. vehicular emissions) would incur a higher cost and energy input, compared to streams with higher CO<sub>2</sub> concentration emissions from a single source (e.g. power plants, refineries and petroleum-based chemicals facilities). The National University of Singapore (NUS) estimated a preliminary aggregated concentration profile for CO<sub>2</sub> emissions in Singapore as shown in Table 2.1.

**Table 2.1: Estimated CO<sub>2</sub> concentration emission profile in Singapore in 2010**

CO <sub>2</sub> concentration (mol %)	Emissions (MT/year)	Example Activity
3	23.7	Natural gas-based power generation
8	13.7	Ethylene cracking from fuel oil Fuel oil-based power generation
15	0.0	Coal-based power plant
20	0.01	Decoking processes
100	0.70	Steam methane reforming, Ethylene glycol plants
TOTAL	38.1	-

As seen in Table 2.1, the bulk of emissions in Singapore comprise low concentrations of CO<sub>2</sub> at about 3 mol %. Compared to many other countries, Singapore's concentration streams are much lower as the majority of our power generation is fuelled by natural gas. The relatively low concentration streams would likely make carbon capture an energetically expensive process. Therefore, it is critical to evaluate and choose the most economical and efficient method for CCS/U. Notwithstanding, most of Singapore's power plants, refineries and petrochemical industries are located in close proximity on Jurong Island. This offers an opportunity to lower the cost of CCS/U through shared facilities.

In the subsequent sections, it is assumed that the baseline emissions that can be captured for Singapore are from the power, refinery, and petrochemical sectors. Emissions streams with nearly 100% CO<sub>2</sub> concentration such as steam methane reforming and ethylene glycol plants are assumed to be already utilised and are excluded. Thus, the baseline emissions used are  $38.1 - 0.71 = 37.4$  MT/year (See Table 2.1) in 2010<sup>2</sup>.

<sup>2</sup> Emissions from non-stationary sources such as emissions from direct fuel combustion from transport are not suitable for CCS/U and are omitted from the calculations of total CO<sub>2</sub> suitable from CCS/U.

### 3. POTENTIAL CCS/U TECHNOLOGIES

CCS/U comprises three main components: capture and concentration, storage and sequestration, and utilisation. The ultimate aim of CCS/U is to reduce CO<sub>2</sub> emitted to the atmosphere. To serve this goal, the captured CO<sub>2</sub> can either be stored in an appropriate and safe way (i.e., sequestration), or converted into useful products (i.e., utilisation). Figure 3.1 illustrates the overall scheme of CCS/U.

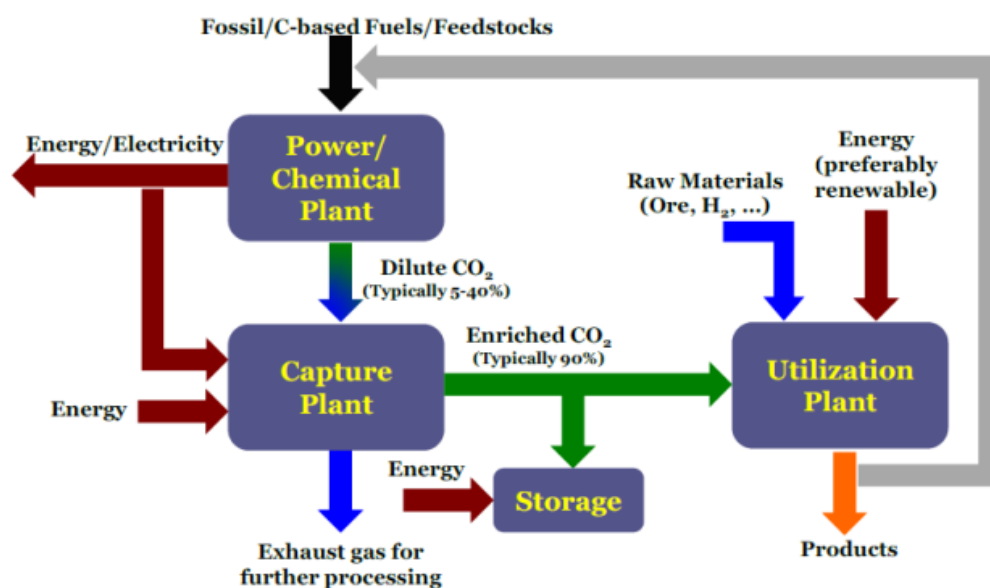


Figure 3.1: Overall scheme of CCS/U

Several technology options are possible for each component, but many are nascent and require further R&D. While there is a multitude of studies and roadmaps on CCS, considerably less work has been done on CCU. Most of the work remains primarily in the domain of academia as CCU is expected to continue playing only a minor role in global carbon mitigation. However, as Singapore faces limitations on viable geological storage, and has an established globally competitive chemicals cluster with the potential to utilise captured carbon (if the technology becomes feasible and cost effective in the longer term), this roadmap will consider CCU together with CCS.

As CCS/U technology is still evolving, a multi-pronged approach involving a mix of options may be required. In addition, the strategy for CCS/U is site and country specific. Hence, any approach for CCS/U in Singapore should take into account our local context and circumstances.



## 3.1 CARBON CAPTURE AND CONCENTRATION (CCC)

### 3.1.1 Modes of CCC

CCC is imperative for subsequent sequestration / utilisation of carbon. There are 3 modes of carbon capture, named after the method of combustion or location of capture in a CO<sub>2</sub>-producing process. These are post-combustion, oxy-combustion, and pre-combustion.

**Post-combustion** involves the capture of CO<sub>2</sub> from the flue gas stream exiting the combustion process. This mode of capture is applicable for most existing power and chemical plants. Since air is used for combustion, the majority of the flue gas is nitrogen, and CO<sub>2</sub> concentrations are low. Thus, the energy for post-combustion capture is the energy required to separate CO<sub>2</sub> from N<sub>2</sub>, moisture, and other contaminants in the flue gas such as SO<sub>x</sub> and NO<sub>x</sub>.

**Oxy-combustion** uses enriched oxygen instead of air for combustion. Thus, one needs to first enrich oxygen from air. The flue gas from such a process has minimal nitrogen content, so oxy-combustion CO<sub>2</sub> capture involves mere condensation of water from the flue gas. Neglecting the energy for this condensation, oxy-combustion capture energy equals the energy required for air separation.

**Pre-combustion** involves gasification of a fossil fuel via enriched oxygen to obtain a mixture of CO and H<sub>2</sub>. This mixture is converted to a CO<sub>2</sub>-H<sub>2</sub> mixture via the water gas shift reaction. H<sub>2</sub> and CO, separated from CO<sub>2</sub>, is combusted to generate heat or power. In contrast to the first two modes, pre-combustion capture involves two separations, but with lower energy requirements. The first is to enrich oxygen from air, and the second is to separate CO<sub>2</sub> from H<sub>2</sub>. Thus, pre-combustion capture energy is the sum of the energies for air and CO<sub>2</sub>-H<sub>2</sub> separations.

The energy required to run a capture process is known as energy penalty. It is perhaps the most objective consideration for the acceptability of a proposed capture technology. However, given the scale of CO<sub>2</sub> emissions, the area footprint and capital costs of a capture plant are also critical. The area footprint is particularly important for retrofitting existing plants with capture units. Thus, the key challenges for carbon capture are energy penalty, plant area footprint, and capital costs. Due to the lack of reliable capital cost data and area requirements, the subsequent analysis will be based on energy penalty alone. In order to compare various capture options and establish practical targets for capture energy, the thermodynamic energy limit was established to determine the minimum work required for CCC.

### 3.1.2 Evaluation of CCC

Assuming that all separations take place at room temperature, and the practically achievable targets for these capture energies ( $E_{\text{target}}$ ) are assumed to be 5 times<sup>3,4</sup> the minimum capture energy<sup>5</sup> ( $E_{\text{min}}$ ) required, Table 3.1 illustrates the energy requirements for the various CCC modes discussed above. A more detailed breakdown of  $E_{\text{min}}$  and capture cost can be found in Appendix A.

**Table 3.1: Target energies (kWh/tonne CO<sub>2</sub>) for CO<sub>2</sub> capture in various modes for different fuels**

Fuel Type	Formula	$E_{\text{target}}$ (kWh/tonne CO <sub>2</sub> ) for CCC				
		Post-combustion	Oxy-combustion	Pre-combustion		
				Air Separation	CO <sub>2</sub> – H <sub>2</sub> Separation	Total
Natural Gas	CH <sub>4</sub>	351	383	95.8	175.9	271.7
Fuel Oil	CH <sub>2</sub>	273	287	95.7	150.3	246.0
Coal	CH	220	240	96.0	131.6	227.6

Besides the absolute energy requirements, it is important to consider energy penalties<sup>6</sup>. Figure 3.2 shows the penalties associated with the various capture modes in power plants using different fuels<sup>7</sup>. The energy penalty is the lowest for (a) natural gas, followed by fuel oil and coal, and (b) pre-combustion, followed by post-combustion and oxy-combustion.

Figure 3.3 compares the utilisation of pre and post-combustion power plants under the current power generation scenario in Singapore. If one were to undertake post-combustion CCC in the existing power plants, then the total CO<sub>2</sub> emissions would be 27.82 MT/year. However, if pre-combustion capture were to be undertaken at these plants, the CO<sub>2</sub> vented would be 23.78 MT/year. In other words, replacing existing power plants with pre-combustion plants would reduce total emissions by 4.04 MT/year as compared to installing post-combustion capture facilities for existing power plants.

<sup>3</sup> Bhowan and Freeman, Analysis and Status of Post-Combustion Carbon Dioxide Capture Technologies, Environ. Sci. Technol. 2011, 45, 8624–8632

<sup>4</sup> [http://folk.ntnu.no/obolland/pdf/GHGT8\\_Review\\_Lecture\\_Olav\\_Bolland.pdf](http://folk.ntnu.no/obolland/pdf/GHGT8_Review_Lecture_Olav_Bolland.pdf)

<sup>5</sup> The minimum capture energy is simply the minimum thermodynamic energy required to separate a gaseous component from its mixture.

<sup>6</sup> For estimating these penalties, power generation efficiency for post- and oxy-combustion based power plants is assumed to be 45%, while that for pre-combustion based power plants is assumed to be 50%. These efficiency numbers do not include the capture penalties.

<sup>7</sup> Energy penalty calculations based on power plant with 500 MW of net outputs

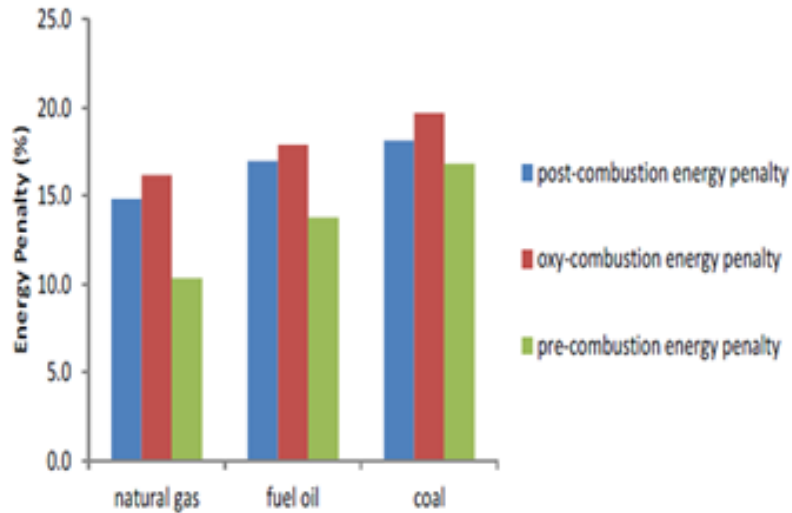


Figure 3.2: Energy penalties for different methods of CO<sub>2</sub> capture

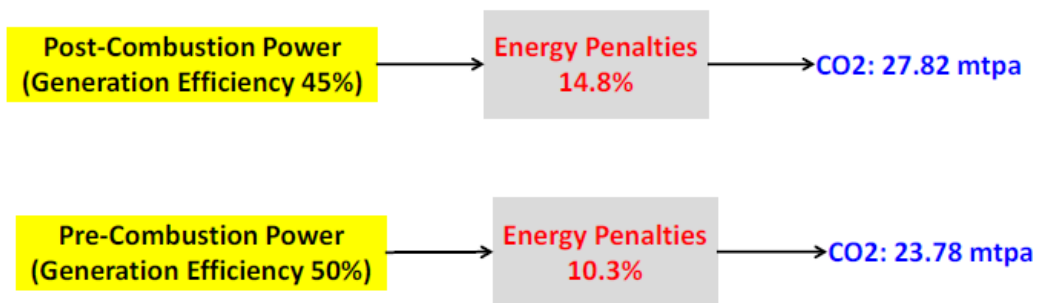


Figure 3.3: Power generation with post-combustion capture vs. pre-combustion capture showing energy penalties and CO<sub>2</sub> emissions

The power, refining and chemical industries need a robust, economical, and compact CCC technology that can be readily retrofitted into the existing plants or implemented in the next-generation plants. For all future greenfield power plant developments, pre-combustion options are attractive based on energy penalties. Additionally, infrastructure costs and adjacent operations may allow for synergistic combinations with the other options, such as oxy-combustion.

### 3.1.3 Technologies for Capture

There are several methods available for the capture of the CO<sub>2</sub> emissions, which can be categorised into physical, chemical or biological pathways. Physical pathways include physical absorption, adsorption, cryogenic separation and low temperature distillation and membrane separation. The large-scale separations technologies such as cryogenic

distillation and amine-based absorption have high energy penalties today. The relatively new adsorption-based and membrane-based separation processes are emerging as energy efficient alternatives for industrial gas separation. All of these technologies are currently heavily researched areas in developed countries as no singular technology has emerged as the most promising solution as yet.

### 3.1.3.1 Carbon capture through physical pathways

#### *Absorption*

In physical absorption, CO<sub>2</sub> is absorbed onto a liquid absorbent which is then regenerated by either heating, pressure reduction, or a combination of both. Physical absorption is well established, with commercial technologies such as Selexol (a liquid glycol-based solvent) and Rectisol (based on low temperature methanol) being used commercially for removing CO<sub>2</sub>. Absorption based capture technology's main challenges are thermal energy penalty due to heating requirements for the regeneration of the solvent, high energy requirements for the operation of pumps and flue gas blowers, degradation of and corrosion due to the solvents. Thus, there is a need to develop high-capacity, low-cost, low-energy, mechanically and thermally robust, non-corrosive, stable against flue gas contaminants, and non-degradable solvents and solids that require much less energy for capture. Additionally, these materials and their associated processes must be integrated well within the CO<sub>2</sub> generating facilities.

#### *Adsorption*

In physical adsorption, CO<sub>2</sub> is adsorbed onto a solid adsorbent set in a bed in a column. Once the bed is saturated with carbon dioxide, another bed is put in its place, while the used bed is regenerated. Different techniques are used to desorb (regenerate) the saturated bed: e.g. Pressure Swing Adsorption (PSA), Temperature Swing Adsorption (TSA) or the Electrical Swing Adsorption (ESA).

Adsorption is still in a nascent stage compared to absorption. The processes are still inefficient and more technological advancement is needed prior to commercialisation. Pilot tests on CO<sub>2</sub> recovery from coal and oil fired power plants show that the energy consumption for an adsorption based capture process is equivalent to a significant loss corresponding to 21% of the energy output from the power plants. Adsorption-based processes also need large amounts of sorbents to handle large quantities of flue gases. Thus, research on efficient adsorption-based capture processes to lower energy penalty is needed. For example, work done at Singapore's A\*STAR Institute of Chemical and Engineering Sciences (ICES) and other international research foresee a potential 10 – 15% energy penalty for adsorption-based capture from coal-fired plants, making it an attractive low-energy alternative to absorption. Further research is required to design and develop

high-capacity, high-selectivity, impurity-resistant (e.g. water, NO<sub>x</sub>, SO<sub>x</sub>), high-density, mechanically strong, and low-energy solid adsorbents.

### *Cryogenic Separation or Low Temperature Distillation*

In cryogenic separation, the exhaust gas (after removal of NO<sub>x</sub> and SO<sub>x</sub>) is cooled to a temperature such that only the CO<sub>2</sub> is liquefied. Given the energy cost of liquefaction, this process is primarily limited to CO<sub>2</sub> concentrations of more than 50%. There is potential to use this process in conjunction with other process technologies such as utilising the cold energy from LNG gasification.

Cryogenic separation processes are well established for separation of air, olefin-paraffin mixtures, natural gas, etc. However, cryogenic separation for CO<sub>2</sub> capture has not been studied much. These processes offer promising synergistic possibilities with other capture technologies described above and opportunities such as the nearby availability of cold energy (e.g. LNG terminal). In contrast to the other capture technologies discussed above, they pose relatively fewer material challenges, but significant process and system-level challenges in terms of process development and intensification and process/energy integration.

### *Membrane Separation*

These processes are normally classified into two categories based on membrane type. One membrane type is the gas separation membrane where the gases are separated by the processes of solution/diffusion because one gas may have greater solubility/diffusivity into and through the semi-permeable polymer membrane, while the others are rejected (blocked.) Transmembrane partial pressure differences are the driving forces for the separation of the gases. The other membrane type involves facilitated transport, where the CO<sub>2</sub> may be facilitated across the membrane by absorbing liquids, such as the amines, on the other side of the membrane and within the pores of a micro- or nano-porous membrane.

Membrane based separation technology is currently limited by the selectivity of currently available membrane materials as well as the high cost of materials. The membranes available today exhibit selectivity in the range of 100 – 150, while a selectivity of more than 200 is required for successful application of membrane-based CO<sub>2</sub> capture processes<sup>8,9</sup>. This inefficiency arises from the low CO<sub>2</sub> partial pressure difference from other gases, resulting in a low driving force for gas separation and higher energy penalties on power generation. The amount of membrane material (thus the capture cost), which is currently expensive, also

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<sup>8</sup> A review of techno-economic models for the retrofitting of conventional pulverised-coal power plants for post-combustion capture (PCC) of CO<sub>2</sub>, Zhao et. al., Energy Environ. Sci., 2013, 6, 25.

<sup>9</sup> B. Metz, O. Davidson, He. De Coninck, M. Loos, L. Meyer (eds.). Carbon Dioxide Capture and Storage, Working Group III, UN Intergovernmental Panel on Climate Change, (IPCC), Cambridge University Press, New York, NY, USA, 2005, Chapter 3

increases linearly with the amount of flue gas. Therefore, there is a clear need for designing new membrane materials that exhibit higher selectivity for CO<sub>2</sub> and are economical.

### **3.1.3.2 Carbon capture through chemical pathways**

Currently, chemical absorption with monoethanolamine (MEA<sup>10</sup>) is the most commonly used method for separating CO<sub>2</sub> from flue gas in commercial projects. Most of the commercial approaches involve about 30% MEA as the scrubbing absorbent for the CO<sub>2</sub> while the other gases are exhausted. The CO<sub>2</sub> must then be separated from the amine, which is recycled. Other chemicals that could be used to scrub out the CO<sub>2</sub> gas include the more sterically hindered amines (ie greater reactivity but more temperature sensitive), ammonia, and potassium or sodium carbonates.

### **3.1.3.3 Carbon capture through biological pathways**

Capture of CO<sub>2</sub> by bio-resources is not commercially viable today but several research groups and academic institutions are currently involved in or seeking funding for R&D projects. An example would be the production of microalgae which captures CO<sub>2</sub> through normal plant photosynthetic processes. In the presence of water, sunlight and CO<sub>2</sub>, microalgae will proliferate which can then be harvested for its lipids and carbohydrates for food, fertiliser, and fuel value. While micro-algae projects may be marine-based or land-based, international projects for the latter outnumber the former. Singapore's limited land area may mean that marine-based algae systems may be worth considering in the longer-term. The key challenge in capture through bio-resources is the algae productivity towards CO<sub>2</sub> uptake. However, most estimates and studies today have been developed on land-based algae systems and not for off-shore systems.

## **3.1.4 Technological Challenges**

As discussed in Section 3.1, there are three major challenges or trade-off factors for an effective capture technology – plant area footprint, energy penalty, and capital costs. These must be addressed simultaneously for any effective capture technology. From a carbon mitigation angle, when assessing the potential of a CCC technology, it is important that the energy penalty incurred does not result in more emissions being emitted.

Currently, with the exception of absorption via MEA, CC technologies are still in their nascent stages and are limited to R&D applications. As a result, estimation of their capital costs and their area footprint is challenging. As a result, energy penalty estimates are preferred when comparing the feasibility of CC technologies today. However, in order to

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<sup>10</sup> MEA is a standard solvent for CO<sub>2</sub> absorption.

determine an effective capture technology, knowledge of these three factors (area footprint, energy penalty and capital cost) are required.

Due to the high cost and high energy requirements of CC technologies, extensive research is required to improve today's processes to obtain desired efficiencies at cost competitive prices. This will include advancement in novel and robust materials (solvents, adsorbents, solids and membranes) for capture processes and development of novel, compact, synergistic and energy efficient processes. Finally, while CC technologies are applied at some large industrial plants, such as natural gas processing and ammonia production facilities, these techniques are not designed for capturing CO<sub>2</sub> from large-scale power plants, the major stationary source of CO<sub>2</sub> emissions in Singapore. Thus, there is a need to develop technologies that can capture and concentrate relatively pure CO<sub>2</sub> (to ~95 mol% concentration) from flue gas streams with low concentrations of CO<sub>2</sub> at a large scale.

### 3.1.5 International Capture Technologies

Table 3.2 indicates the capture technologies associated with several commercial CCS projects around the world. The Mongstad project in Norway stands out as a good case study for Singapore as the emissions profile, from a natural gas power plant and a refinery catalytic cracker, is similar to emission sources in Singapore. The Mongstad project utilises post combustion technology and tests an amine based CO<sub>2</sub> capture technology and a chilled ammonia-based technology. Actual test operations in Mongstad commenced in 2012 and monitoring of their progress would be useful. Most of the other CCS plants are developed for the capture of CO<sub>2</sub> from gas fields, rather than from power plants or refineries, as would be the case for Singapore.

**Table 3.2: Capture technologies used by various plants across the world**

Current Projects in CCS				
Plant	Location	Capture Technology	Incoming CO <sub>2</sub> concentration	Type
Sleipner	Norway	Amine Absorption	9%	Commercial
Snohvit	Norway	Methyl Diethylamine	5 – 6%	
Weyburn-Midale	Canada	Lurgi coal gasification	4.5%	
In Salah	Algeria	Methyl Diethylamine	4 – 9%	
Mongstad	Norway	Amine/Chilled Ammonia	3.5% (gas)/13% (refinery)	Experimental/ Demonstration
CATO-2/K12-B	Netherlands	Post/Pre/Oxy	13%	
SE Region Seq. Project	USA	Chilled Ammonia	13%	

Most of the international studies and roadmaps focus on the capture of relatively high concentration CO<sub>2</sub> emissions (as high as 14%) primarily from post-combustion of oil- and coal-fired power and steam plants because they constitute over 80% of the point source emissions. However for Singapore, the majority of our emission streams tend to be of lower concentration (3%) (See Section 2) due to power generation from mostly natural gas.

### 3.2 STORAGE AND SEQUESTRATION

Storage and sequestration refer to the process of long term storage of CO<sub>2</sub> after it has been captured and concentrated from various sources. In geological sequestration, the captured and concentrated CO<sub>2</sub> stream is compressed, transported to, and then stored in suitable geological sites. The potential geological sites used for the long-term storage of CO<sub>2</sub> include depleted oil and gas reservoirs, spent coal seams, deep saline formations, and oceans. In comparison to utilisation, CCS is more economical and there have been more research and demonstration sites dedicated to this.

The key consideration in sequestration is that the sequestered CO<sub>2</sub> does not escape into the atmosphere. Therefore, it is desirable to assess and verify the suitability of a site for environmental safety and long term integrity. A detailed assessment and verification of the risks associated with a site is required.

Expanding on Table 3.2, Table 3.3 shows the types of storage and sequestration undertaken at each site.

**Table 3.3: Method of storage and sequestration for CCS projects across the world**

Plant	Location	Storage & Sequestration
Sleipner	Norway	Off-shore gas concentration and injection into saline aquifer above the Sleipner gas field
Snohvit	Norway	Gas from LNG plant on-shore pumped back via CO <sub>2</sub> pipeline back into saline aquifer in the Snohvit field
Weyburn – Midale	Canada	CO <sub>2</sub> from gas field [umped back into deep underground saline aquifer
In Salah	Algeria	NO storage. Test site for capture from CHP plant and from refinery cracker
Mongstad	Norway	CATO-2 (11 test/demo sites); K12-B (Sequestration into same gas field)
CATO-2/K12-B	Netherlands	Storage in saline aquifer above the Citronella oil field
SE Region Seq. Project	USA	Sequestration in saline Mount Simon Sandstones



Most of the CCS projects today are undertaken at gas fields. They are not reflective of the challenges for capture, storage and sequestration of CO<sub>2</sub> from power plants or refineries. For gas field sites, CO<sub>2</sub> emitted from the gas fields and their activities are stored and sequestered in-situ in geological formations, thereby minimising transportation costs. The CO<sub>2</sub> injected are also of high concentrations of 95% to 100%. This implies that the capture costs associated with these projects need to be scaled up when estimating costs for capturing emission streams with lower CO<sub>2</sub> concentration. Hence, for countries with limited local geological storage options and/or low CO<sub>2</sub> concentration streams, such as Singapore, the cost for storage, transport and sequestration is expected to be higher.

An example of an innovative CO<sub>2</sub> storage strategy is a CO<sub>2</sub> Hub, such as that seen in Rotterdam<sup>11</sup>. At this facility, CO<sub>2</sub> from multiple sources are concentrated and accumulated in a CO<sub>2</sub> Hub, which serves as an interim onshore storage facility. The concentrated CO<sub>2</sub> could then be utilised or sequestered.

### 3.2.1 Economics of CCS in Singapore

There are several factors affecting the economics of a CCS project: CO<sub>2</sub> source, distance between the capture and storage sites, transportation mode, and characteristics of the storage site. Offshore storage is usually more expensive than onshore storage due to higher costs involved in survey, construction, and operation. As a general rule, 60% to 80% of costs are related to capture and concentration of CO<sub>2</sub>, while the remaining is evenly split between transportation and storage. Table 3.4 illustrates costs of CO<sub>2</sub> transport and storage varying over a range depending on the location and methods.

**Table 3.4: CO<sub>2</sub> transport and storage cost estimates (international)**

	Method	Location	Cost (\$/tonne CO <sub>2</sub> )
<b>CO<sub>2</sub> Transport</b>	Pipeline	Onshore	2-7
		Offshore	5-13
	Ship		13-20
<b>CO<sub>2</sub> Storage</b>	Saline Aquifers	Onshore	3-15
		Offshore	8-26
	Depleted Oil and Gas Fields	Onshore	1-9
		Offshore	3-18

<sup>11</sup> CO<sub>2</sub> capture and storage in Rotterdam, Rotterdam Climate Initiative, May 2011.

Table 3.5 illustrates the estimated cost for post combustion CCS of Singapore’s emissions, based on onsite sequestration at a suitable storage site. (see Appendix B for calculations and other assumptions). Singapore will need to transport CO<sub>2</sub> to regional locations for storage, which will cost an additional \$0.06/tonne/km based on pipeline transportation. For longer distances, transportation by shipping would be more cost effective than pipeline.

**Table 3.5: CCS cost estimate (\$/tonne CO<sub>2</sub>) and target reduction plans for Singapore**

2011 Emissions		2015		2030		2050	
% CO <sub>2</sub> Stream	Amount mtpa (%)	Reduction % (mtpa)	Cost \$/tonne (Total M\$)	Reduction % (mtpa)	Cost \$/tonne (Total M\$)	Reduction % (mtpa)	Cost \$/tonne (Total M\$)
3	23.7 (50.9)	0 (0.0)	228 (0)	15 (3.5)	155 (543)	40 (9.4)	93.5 (879)
8	14.0 (30.4)	5 (0.7)	193 (135)	20 (2.8)	131 (367)	50 (7.0)	79 (533)
15	0.00 (0.00)	40 (0.0)	169 (0.0)	80 (0.0)	115 (0.0)	80 (0.0)	69 (0.0)
20	0.01 (0.02)	50 (0.005)	158 (0.79)	80 (0.008)	107 (0.86)	90 (0.009)	65 (0.59)
100	0.71 (1.54)	80 (0.57)	70 (40)	95 (0.68)	48 (33)	95 (3*)	29 (87)
<b>Total</b>	<b>38.12</b>					<b>19.4 mtpa (51%)</b>	<b>(\$1520M) (\$78.4/tonne CO<sub>2</sub>)</b>
<b>* Assume additional 2.4 mtpa from an incoming (industry) plant for 100% stream</b>							

Due to its geographical constraints, Singapore will have to explore options in the region and beyond should it decide to proceed with sequestration, taking into account the economic costs and potential political implications. For example a detailed analysis of geological storage potential has been done by Thailand and Indonesia<sup>12,13</sup>. It was reported that of the 94 sedimentary basins in Thailand, 10 alone are capable of holding approximately 9 GT CO<sub>2</sub>. The economic feasibility of CCS, related regulations and incentives, establishment of further capacity and injectivity, risk assessment and uncertainties are currently being investigated in Thailand.

<sup>12</sup> Maneeintr, K, Carbon capture and storage/utilisation in Thailand, Presented at NCCS Workshop 2 on CCS/U roadmap, November 26, 2012, Singapore.

<sup>13</sup> Indonesia CCS Study Working Group. 2009. Understanding Carbon Capture and Storage Potential in Indonesia. [https://ukccsrc.ac.uk/system/files/publications/ccs-reports/DECC\\_CCS\\_117.pdf](https://ukccsrc.ac.uk/system/files/publications/ccs-reports/DECC_CCS_117.pdf)

### 3.2.2 Technological Challenges

Lack of storage sites close to the emission sources and the high costs associated with the long-distance transport of CO<sub>2</sub> are some of the current limiting factors to the deployment of CCS for Singapore. Currently, the estimated cost of CCS for Singapore ranges from \$70 – 228/tonne (Table 3.5). Given efficiency gains in future, these costs may drop to \$29 – 94/tonne in 2050 which would make it more economically attractive. However, since CCS is an investment without returns (in the absence of a carbon price), cost of power plants equipped with capture technology would increase, which would in turn increase the cost of electricity. In order to minimise the impact of CCS on electricity cost, RD&D will be required to lower the cost and increase the efficiency of CCS. Long-term monitoring and verification of storage sites, related activities and CCS demonstration projects would also be useful to ensure that stored CO<sub>2</sub> does not escape into the atmosphere.

### 3.3 UTILISATION

Although carbon utilisation (CU) is more technically challenging and more nascent than CCS, CU for fuels and value-added chemical production is slowly receiving attention in the global research landscape. Part of the reason may be due to the uncertainty of the long term consequences and risks of CCS as well as the potential value of products from CU. For Singapore, CU assumes greater importance due to the geological limitations for CCS. Currently, the use of CO<sub>2</sub> for Enhanced Oil Recovery (EOR) and Enhanced Coal Bed Methane Recovery (ECBMR) are the only options under consideration in many of the international reports. However, as these are not applicable in Singapore, other utilisation options such as innovative reactions to convert CO<sub>2</sub> into useful products (fuels, value-added chemicals, building and construction materials, etc.) via organic, inorganic, or biological pathways are explored for Singapore.

In this section, broad perspectives for carbon utilisation are presented based on hydrogenation via renewable hydrogen or natural gas, mineralisation, biochemical conversion, Enhanced Oil Recovery (EOR), Enhanced Coal Bed Methane Recovery (ECBMR), and electrochemical utilisation to formic acid. Various strategies of CCU are discussed and potential carbon mitigations are estimated based on the assumption of 37.4 MT/year of CO<sub>2</sub> emissions from the power, refining and petrochemical sectors of Singapore (see Section 2). Figure 3.4 illustrates the various possible routes of CO<sub>2</sub> utilisation, which will be discussed in the subsequent sub-sections.

It should be noted that for a highly stable molecule such as CO<sub>2</sub>, considerable energy inputs, novel catalysts and processes and high-energy reactants (e.g. hydrogen) are required for its conversion. In addition to energy, several material resources (e.g. water, air, minerals,

microalgae) may also be required to enable carbon utilisation for both hydrogenation and non-hydrogenation pathways.

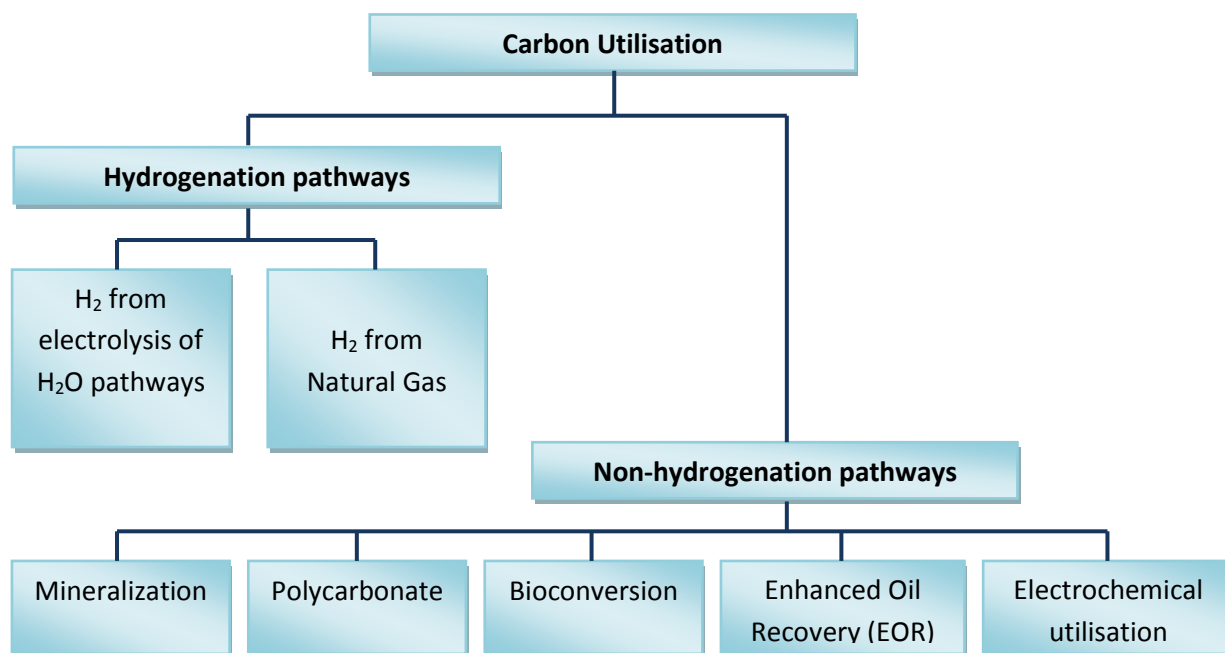


Figure 3.4: Possible routes for CO<sub>2</sub> utilisation

### 3.3.1 Carbon Utilisation via hydrogenation pathways

CO<sub>2</sub> transformation via hydrogen is dependent on the source and cost of hydrogen. Since the aim is to reduce CO<sub>2</sub> emissions, it is desirable to use a renewable source of hydrogen.

#### 3.3.1.1 Hydrogen from renewable sources

Hydrogen can be generated via the electrolysis of water, which is an energy intensive process. Based on the highest achievable efficiency of 73%<sup>14</sup>, power consumption of water electrolysis is 53 kWh/kg. To ensure a net zero carbon emission, it is important that energy used for electrolysis is derived from renewable sources. In the case of Singapore, the main renewable is solar energy. Given that Singapore has a technical potential of approximately 14.9 TWh<sup>15</sup> of solar energy generated from solar PV, the potential amount of hydrogen produced would be approximately 0.29 MT/year.

<sup>14</sup> Olah et al., J. Org. Chem. 2009, 74, 487–498

<sup>15</sup> Solar PV Roadmap 2014. 14.9 TWh solar energy generated in 2050 based on accelerated scenario.

### 3.3.1.2 Products from reacting CO<sub>2</sub> with hydrogen

Several chemicals can be produced by reacting CO<sub>2</sub> with hydrogen. In this study, the chemicals that have been considered include methanol, dimethyl ether (DME), ethylene, natural gas, and formic acid. The stoichiometric reactions representing the conversion of CO<sub>2</sub> to these chemicals along with their heats of reaction are listed below:

- a) Methanol:  $\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$   $\Delta\text{H} = -0.049 \text{ GJ/kmol}$
- b) DME:  $2 \text{CO}_2 + 6\text{H}_2 \rightarrow \text{CH}_3\text{OCH}_3 + 3\text{H}_2\text{O}$   $\Delta\text{H} = -0.061 \text{ GJ/kmol}$
- c) Ethylene:  $2 \text{CO}_2 + 6\text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{OH} + 3\text{H}_2\text{O}$   
 $\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_2\text{CH}_2 + \text{H}_2\text{O}$ ,  $\Delta\text{H} (\text{overall}) = -0.040 \text{ GJ/kmol}$
- d) Methane:  $\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$   $\Delta\text{H} = -0.16 \text{ GJ/kmol}$
- e) Formic acid:  $\text{CO}_2 + \text{H}_2 \rightarrow \text{HCOOH}$   $\Delta\text{H} = 0.015 \text{ GJ/kmol}$

**Error! Reference source not found.** Figure 3.5 illustrates the production of various fuels/chemicals using solar hydrogen (hydrogen produced from electrolysis fuelled by electricity from solar energy). The fuels and chemicals in Figure 3.5 cannot be produced simultaneously and should be viewed as mutually exclusive. Therefore, the production of formic acid offers the highest CO<sub>2</sub> abatement potential at approximately 4 MT/year. However, the abatement of 4 MT CO<sub>2</sub>/year corresponds to a production of 6.2 MT of formic acid/year, which far exceeds the global demand for formic acid (0.72 MT/year). Hence, there is a limitation to the production of formic acid.

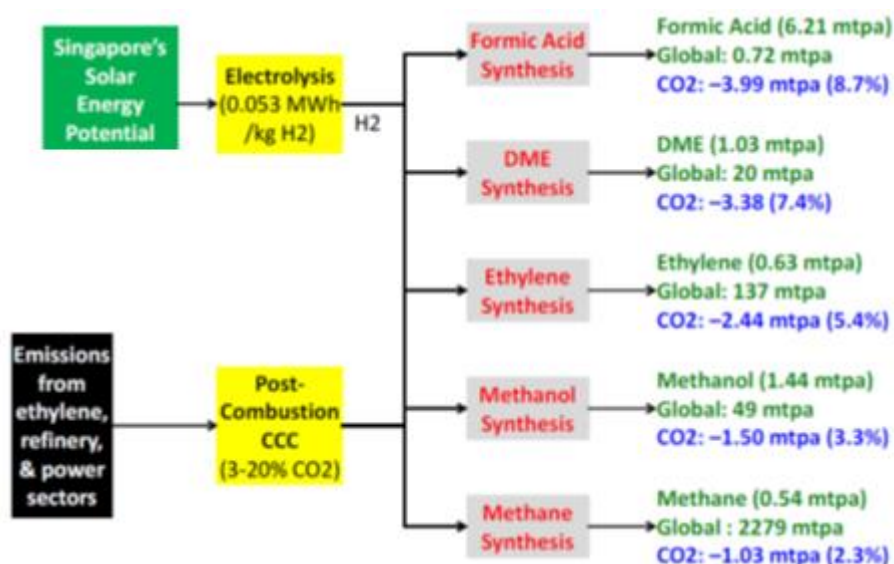


Figure 3.5: Fuels/chemicals production from CO<sub>2</sub> utilisation via hydrogen using Singapore's solar energy

In contrast to formic acid, the world demand for other chemicals suggest the potential for producing them in Singapore through CCU. If more hydrogen could be produced from solar, then more CO<sub>2</sub> could be converted to produce ethylene, methanol, and methane without flooding the market. In addition to the CO<sub>2</sub> reduction estimates, the economics of the

various options were also considered. The cost of chemical utilisation via hydrogenation pathways is based on the following equation:

$$\begin{aligned}
 & \textit{Cost of chemical production} \\
 & = [\textit{Market price of product} + \textit{Carbon tax}] \\
 & - [\textit{H}_2\textit{price} + \textit{CCC cost} + \textit{chemical production cost} \\
 & + \textit{energy cost for producing chemical}]
 \end{aligned}$$

In order to be cost effective, the cost of chemical production via hydrogenation pathway would need to be lower than the market price. The commercial prices for the various products in Table 3.6 are obtained from the literature, while Table 3.7 gives the break-even prices for solar hydrogen for producing formic acid, ethylene, methanol, and methane. It also represents the target that future R&D should achieve to make CO<sub>2</sub> utilisation viable. On the basis of these price targets, methanol seems to be the most favourable chemical, followed by formic acid, ethylene, and dimethyl ether. To bring this into perspective, the current solar hydrogen price would be approximately \$37.1/kg. The production of methane does not seem attractive given the high carbon price and zero/negative hydrogen prices required to break even.

**Table 3.6: Market price (\$/kg) and Break-even hydrogen price (\$/kg) under various Carbon price (\$/tonne) scenarios**

Chemical	Breakeven Solar Hydrogen Price (\$/kg)				Market price (\$/kg)
	No Carbon Price (CP)	CP \$25/tonne	CP \$100/tonne	CP \$200/tonne	
<b>Methanol</b>	3.30	3.32	3.37	3.44	5.26 <sup>16</sup>
<b>Formic Acid</b>	2.43	2.48	2.62	2.80	1.20 <sup>17</sup>
<b>Ethylene</b>	0.19	0.22	0.31	0.42	1.19 <sup>18</sup>
<b>Dimethyl Ether</b>	0.11	0.14	0.26	0.42	0.63 <sup>19</sup>
<b>Methane</b>	-0.09	-0.08	-0.04	0.00	0.13 <sup>20</sup>

Figure 3.6 illustrates the production of chemicals (assuming unlimited hydrogen supply, e.g. through imports) in order to meet only Singapore's domestic chemical industry demands.

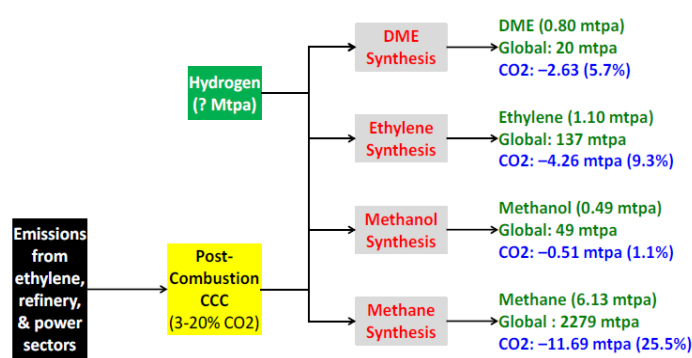
<sup>16</sup> Dolan G., Why methanol is a reliable fuel, 2011

<sup>17</sup> Agarwal et al., Chem Sus Chem 2011, 4, 1301-1310

<sup>18</sup> Platts global petrochemical index in 2010

<sup>19</sup> Based on China market price in 2010

<sup>20</sup> www.indexmundi.com



**Figure 3.6: Fuels/chemicals via unlimited hydrogen for Singapore’s chemical demands**

It can be seen that methane has the highest demand, both locally and internationally, which translates to the highest abatement potential with 11.7 MT CO<sub>2</sub> abatement/year (Figure 3.6). It can be seen that for these chemicals, the global demand for them outweighs local demand. Hence there is a technical potential for Singapore to import hydrogen to process all of Singapore’s emissions to chemicals for exports internationally. However, the issues of obtaining low cost and low energy penalty sources of hydrogen, among others, remain challenges that need to be overcome.

### 3.3.1.3 Technical Challenges for renewable hydrogen production

One of the key challenges is the limited renewable energy available for hydrogen production due to the limited land area available for solar PV deployment in Singapore. There is a need to prioritise the usage of this renewable energy – for hydrogen production or direct use of electricity by other users such as buildings.

The primary challenges of producing hydrogen by using solar energy, are to develop materials with the required electronic properties that have a long lifetime, and to maximise photon utilisation efficiencies. There are 4 main systems that can generate hydrogen via this process:

1. Single reactor filled with water-splitting nano-particle photocatalysts
2. Dual reactor system where the production of H<sub>2</sub> and O<sub>2</sub> from water splitting occurs in different reactor, with a mechanism to transfer H ions between the reactors.
3. Fixed array with a PV/PEC<sup>21</sup> cell immersed in electrolyte
4. Solar collector coupled with a high efficiency multi-junction PV/PEC cell

For systems 1 & 2, the challenge lies in developing the right material: the development of cheap and stable nanoparticle catalysts with desired band gap and catalytic properties, as well as their large-scale fabrication and environmental impact. In addition, for system 2, the

<sup>21</sup> Photoelectrochemical (PEC) cell are solar cells that produce electrical energy or hydrogen in a process similar to the electrolysis of water

development of efficient ion transfer systems between the reactors could be an additional challenge. For systems 3 & 4, the PV cell-based systems would benefit from the development of an efficient low cost solar cell. However, they are still not economical compared to the photocatalyst-based reactors. Here, the development of thin-film low-cost PV materials is a key factor, since large PV surface areas are required.

For the electrolysis of water, the development of cheaper catalysts to replace platinum based catalysts is required. The key challenge is to develop stable and cheap oxygen evolving catalysts that work under actual conditions (sea-water, etc). Beyond the electrocatalysts are the membrane separators for the electrochemical cells: asbestos-based supports impregnated with potassium hydroxide (KOH) or perfluorinated ionomers. The former option poses environmental challenges while the latter is extremely costly (approaching US\$ 1,000/m<sup>2</sup> in some instances). Further R&D is needed to reduce the costs of such electrolysis cells.

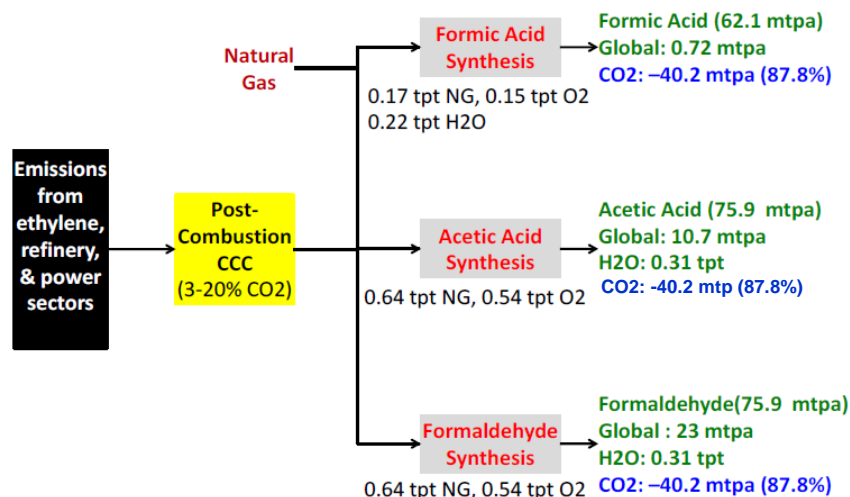
#### 3.3.1.4 Hydrogen from Natural Gas

The predominant source of hydrogen around the world today is natural gas. Since the price of hydrogen from solar is still high compared to the current price of hydrogen, it would make more economic sense to yield hydrogen from natural gas instead of through solar hydrogen. Some examples of products when methane reacts with CO<sub>2</sub> are formic acid, formaldehyde and acetic acid. These are low energy chemicals with maximum hydrogen: carbon (H/C) ratio of 2 and bulk chemicals with wide-ranging uses. Formic acid is used extensively in the tanning, agriculture, pharmaceuticals, and food industries. Formaldehyde is used in the construction, automotive, and furniture industries. Acetic acid is used in the production of chemical compounds such as vinyl acetate monomer, acetic anhydride, and ester.

The productions of formic acid, formaldehyde, and acetic acid from CO<sub>2</sub> and methane involve reactions that are common with Gas to Liquid Technology (GTL), which is an interesting route for the synthesis of important chemicals made from H<sub>2</sub> and CO (syngas). The ratio of H<sub>2</sub> and CO required in GTL varies with the specific chemical being synthesised. However, for all the products, the generation of syngas is the most expensive and energy intensive step. The traditional technology for syngas production is steam reforming (SR), which suffers from the drawbacks of high energy requirements and capital costs. Autothermal reforming (ATR) is recognised as an alternative to SR owing to its advantages such as relative compactness and lower capital costs. In this process, the hydrocarbons are completely converted into a mixture of H<sub>2</sub> and CO in a single reactor. Partial oxidation of the hydrocarbon feed supplies the heat required for the endothermic reforming reactions, thus making the process autothermal.



The use of natural gas for hydrogen will require energy and emit additional CO<sub>2</sub>. Figure 3.7 illustrates the production of chemicals using hydrogen from natural gas, assuming that all additional CO<sub>2</sub> emissions are fully utilised to produce the desired product (i.e. emission feedback into feedstock).



**Figure 3.7: Fuels/chemicals production from CO<sub>2</sub> utilisation via hydrogen from natural gas**

From Figure 3.7, it can be seen that the production of any chemicals from Singapore’s captured emissions, in addition to emissions from processing activities, far exceeds the global demand. Table 3.8 illustrates the break-even costs of making these chemicals under various carbon price scenarios. Formic acid allows the highest production cost, followed by acetic acid and formaldehyde. Even if the cost of producing 1 tonne of formic acid from CO<sub>2</sub> was as high as \$1,085, it is still possible to produce formic acid at its current market price. However, there remains the limiting factor of supply exceeding demand.

**Table 3.8: Break-even production cost (\$/tonne) for various chemicals from CO<sub>2</sub> utilisation using hydrogen from methane under zero emissions scenarios for different carbon price rates**

Carbon Tax (\$/tonne)	0	25	100	200
Formic Acid	1085	1100	1144	1203
Formaldehyde	35	47	83	131
Acetic Acid	301	313	349	397

### 3.3.1.5 Technological challenges for CCU via hydrogenation pathways

CO<sub>2</sub> hydrogenation to methanol and to liquid fuels offers the highest potential for CO<sub>2</sub> abatement. Methanol can be economically converted to small olefins, the building blocks of

the petrochemical industry, through the well-established MTO process. Methanol can also be blended with gasoline to boost octane numbers (methanol has an octane rating of about 110). There might be niche markets to convert alkanes and CO<sub>2</sub> to carboxylic acids (R-H + CO<sub>2</sub> → R CO<sub>2</sub>H). In particular the conversion of ethylene and CO<sub>2</sub> to acrylic acid might be economically promising if a suitable catalyst and process can be developed. Initially promising results with Ni-based homogeneous catalysts have been reported.

The challenges for methanol and fuel synthesis from CO<sub>2</sub> and H<sub>2</sub> are different. Methanol yields are thermodynamically limited at temperatures where modern state-of-the-art copper/zinc oxide, aluminium oxide (Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>) catalysts are active. On the other hand, commercial Fischer-Tropsch catalysts for clean fuel synthesis are unable to rapidly activate CO<sub>2</sub> and catalyse chain growth and make liquid fuels, so the main product is methane. For both reactions, new catalysts and promoters need to be developed, though the challenges for liquid fuel synthesis from CO<sub>2</sub> appear larger. In the case of methanol synthesis from CO<sub>2</sub>, significant progress has been made, and commercial plants that are economically comparable (within a factor 2) with classical large-scale methanol plants are beginning to appear. Key challenges are to improve catalyst activity and stability for the Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> based system and to understand the mechanism and the kinetics for this reaction.

### 3.3.2 Carbon Utilisation via non-hydrogenation pathways

Besides EOR and ECBMR, there are other utilisation options that do not require hydrogen. These are mineralisation, polycarbonation, biochemical conversion via microalgae, and electrochemical conversion. Mineralisation and polycarbonation of minerals and propylene oxide with CO<sub>2</sub> can produce useful products. The bioconversion process is based on the photosynthetic conversion of CO<sub>2</sub> into biomass that can be processed to obtain biofuels and several value-added products such as pharmaceuticals, nutraceuticals, etc. The electrochemical method involves the reduction of CO<sub>2</sub> to chemicals such as formic acids or formate salts.

#### 3.3.2.1 Mineralisation

CO<sub>2</sub> mineralisation comprises a chemical reaction between suitable minerals and CO<sub>2</sub>. The CO<sub>2</sub> is effectively sequestered as a mineral such as carbonate which is stable on geological timescales. One option is to use a mineral such as serpentine to produce silica (sand). These are useful materials for building and construction industries. It should be noted that mineralisation in Singapore poses additional challenges due to the large amount of land area required to store the raw material. There may also be additional emissions locally due to the energy use in mineralisation which would otherwise be avoided as mineralisation products are usually imported. The annual demand for sand in Singapore is approximately

14.2 MT/year and gravel (MgCO<sub>3</sub>) is approximately 30.8 MT/year. In order to determine the net CO<sub>2</sub> avoided, the following equation was used:

$$\begin{aligned}
 \text{Net Energy Avoided} &= \text{Stoichiometric energy consumed} \\
 &- [\text{Energy consumption from (CCC + mineralization)}]
 \end{aligned}$$

The energy consumption for mineralisation is 5.8 GJ/tonne CO<sub>2</sub> or 0.8 tonne CO<sub>2</sub> emission/tonne. However, the form of energy required for this makes a significant difference in the CO<sub>2</sub> emissions avoided – utilising energy (for the extraction and recovery of ammonium sulphate) in the form of heat (from natural gas) would equate to 8.1 MT/year CO<sub>2</sub> emissions avoided as compared to 0.4 MT/year CO<sub>2</sub> if energy in the form of electrical power was used. Table 3.9 shows the reduction in CO<sub>2</sub> emissions using these two energy sources.

**Table 3.9: Reductions in CO<sub>2</sub> emissions using mineralisation**

Process	Stoichiometric CO <sub>2</sub> Consumption (MT/year)	Net CO <sub>2</sub> Avoided (MT/year)	CO <sub>2</sub> Avoided (tonne CO <sub>2</sub> /tonne produced)
Mineralisation (using heat from NG)	15.6	8.1	0.57
Mineralisation (using power)	15.6	0.4	0.03

### 3.3.2.2 Polycarbonate

An option for CCU is to use propylene oxide to produce propylene carbonate and convert it to polycarbonate. The annual demand of polypropylene in Singapore is approximately 1.01 MT/year<sup>22</sup>. The calculations to yield the net energy avoided is the same as that for mineralisation and the net CO<sub>2</sub> avoided is shown in Table 3.10. For polycarbonate, the reaction between propylene oxide and CO<sub>2</sub> results in a net generation of CO<sub>2</sub> and is hence undesirable.

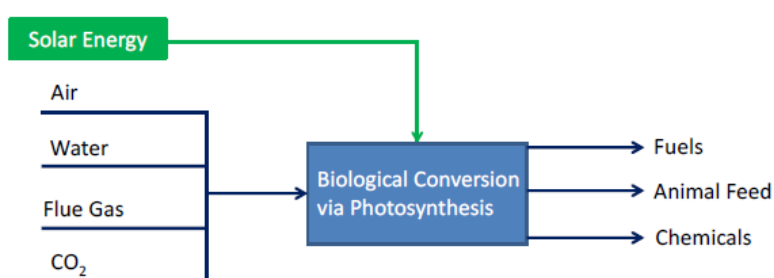
<sup>22</sup> ExxonMobil contributes 405 ktpa ([www.exxonmobil.com.sg](http://www.exxonmobil.com.sg)) and Shell contributes 600 ktpa ([www.shell.com.sg](http://www.shell.com.sg))

**Table 3.10: Reductions in CO<sub>2</sub> emissions using polycarbonate**

Process	Stoichiometric CO <sub>2</sub> Consumption (MT/year)	Net CO <sub>2</sub> Avoided (MT/year)	CO <sub>2</sub> Avoided (tonne CO <sub>2</sub> /tonne produced)
Polycarbonation	0.43	-0.16	-0.16

### 3.3.2.3 Biochemical Conversion via Microalgae

CO<sub>2</sub> can be sequestered and used in the form of biofuel production. Figure 3.8 illustrates the schematic of bioconversion process for CO<sub>2</sub>.



**Figure 3.8: Biological pathways for the utilisation of CO<sub>2</sub>**

There are several variety of crops from which biofuels can be produced (Table 3.11). Among these, microalgae offer several advantages such as higher growth rates, low nutrient and land requirements. Microalgae consume CO<sub>2</sub> in the presence of water, sunlight, and other nutrients to form algal biomass that consists of various components such as carbohydrates, lipids and proteins. The lipids content can be extracted and processed to obtain biofuels, and the remaining biomass can be used for value-added products such as nutraceuticals, pharmaceuticals, etc.

**Table 3.11: Land Area Yields for Biofuels Production from Various Crops<sup>23</sup>**

Crop	Oil Yield (L/1000 km <sup>2</sup> )
Soybean	44.6
Canola	119
Jatropha	189
Coconut	269
Oil Palm	595
Microalgae	5,870

Despite microalgae needing the least land area among the other types of biofuels, the land area required is still large and would be a limiting factor, especially in a land scarce Singapore. To illustrate, in order to capture Singapore's current emissions of 45.8 MT/year

<sup>23</sup> Wilcox, Carbon capture, Springer 2012

via microalgae, approximately 3,400 km<sup>2</sup> of area would be required – about 4.5 times the area of Singapore.

### Biofuels from Microalgae

Microalgae can be processed into various biofuels. In this analysis, the production of three biofuels is considered: biodiesel, bioethanol and biomethane. Figure 3.9 shows the impact of using 10% of Singapore’s land area for the cultivation and processing of microalgae to produce biodiesel, bioethanol, and biomethane from CO<sub>2</sub> and solar energy in Singapore (calculations and assumptions in Appendix C).

Not factoring resource requirements such as water and separation energy required for microalgae cultivation, we can see that the total CO<sub>2</sub> mitigated from the generation of biofuels from microalgae ranged from 0.3 – 0.4 MT/year. Considering this requires 10% of Singapore’s land area, utilising the equivalent land area for solar PV deployment would yield approximately 7.5 MT CO<sub>2</sub> abatement. Hence, utilising the land for other resources such as solar PV would be more beneficial in terms of CO<sub>2</sub> abatement as compared to microalgae production. It can also be seen that the production of microalgae in Singapore has marginal impact on CO<sub>2</sub> mitigation compared to the resources required.

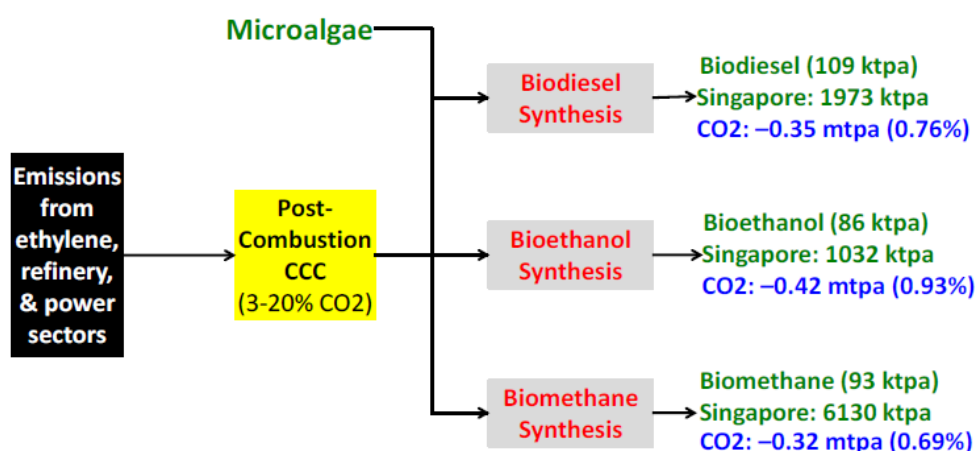


Figure 3.9: Photosynthetic conversion of CO<sub>2</sub> into biofuels via microalgae

### Value-Add Products from Microalgae

Utilising microalgae for biofuels is currently unattractive owing to the high capital, operating, and maintenance costs associated with the cultivation and processing of microalgae in comparison to conventional fossil fuels. In contrast, products like nutraceuticals and pharmaceuticals are able to offset high production costs because of their niche markets and high prices. Thus, although the impact on mitigation is small, they may offer some niche and attractive options for CO<sub>2</sub> utilisation from an economic perspective.

This is evident from the market prices of some products that are currently produced from microalgae, which are about three orders of magnitude higher than the current average gasoline price of \$0.10 /g in the USA. Further research is required to improve the productivity, yields, efficiency, and economics, before microalgae systems can be economical for biofuels and make significant contribution to mitigation efforts.

**Table 3.12: Market price of various microalgae products**

Microalgae	Producer	Production (ton/dry wt)	Price US\$/g *	Application
Spirulina	China, India, US, Myanmar, Japan	3000	60	Nutrition, Cosmetic
Chlorella	Taiwan, Germany, Japan	2000	60	Nutrition, Cosmetic
Chlorella	Taiwan, Germany, Japan	2000	90	Aquaculture
Dunaliella salina	Australia, Israel, US, Japan	1200	350-3500	Nutrition, Cosmetic
Haematococcus pluvialis	India, Israel, US	300	90	Aquaculture
Cryptocodinium cohnii	US	240	70	DHA Oil
Shizochytrium	US	10	70	DHA Oil

### 3.3.2.4 CO<sub>2</sub> Utilisation for Enhanced Oil Recovery (EOR)

EOR is a process by which residual crude oil from oil fields is extracted in conventional oil production processes by injecting a fluid such as water and CO<sub>2</sub>. The injected CO<sub>2</sub> makes the oil swell and less viscous, which enables easier flow through the porous rock media. While some of the injected CO<sub>2</sub> remains inside the reservoir, the rest comes out with the oil, and is re-injected. After the petroleum reservoir is depleted completely, CO<sub>2</sub> can be stored inside for the long-term. EOR is considered a form of CO<sub>2</sub> utilisation and CO<sub>2</sub> can be sold for EOR.

This is perhaps the most attractive option for CCU currently and is the primary use of CO<sub>2</sub> in the USA, accounting for the removal of approximately 55 MT CO<sub>2</sub>. In the USA, the EOR industry has demonstrated successful injection of CO<sub>2</sub> into oil reservoirs over three decades. Table 3.13 shows the major EOR sites in USA using CO<sub>2</sub>.

**Table 3.13: CO<sub>2</sub> Utilisation via EOR in the US**

Location	CO <sub>2</sub> Sources	CO <sub>2</sub> Supply (MT/yr)	
		Natural <sup>24</sup>	Anthropogenic <sup>25</sup>
W.Texas/New Mexico/Arizona	Colorado/New Mexico; gas processing plant (West Texas)	32.0	1.98
Colorado/Wyoming	Gas processing plant (Wyoming)	-	4.33
Mississippi/Louisiana	Mississippi	13.0	-
Michigan	Ammonia plant (Michigan)	-	0.28
Oklahoma	Fertiliser plant (Oklahoma)	-	0.56
Saskatchewan	Coal gasification plant (North Dakota)	-	2.83
Total (Mt CO <sub>2</sub> )		45	10

EOR may be feasible for Singapore if CO<sub>2</sub> can be successfully captured, concentrated and transported to the several oil and gas reservoirs in the region. Table 3.14 illustrates case studies of CO<sub>2</sub> mitigation and EOR cost at three reservoirs – Sarawak (Malaysia), East Kalimantan (Indonesia), and South Sumatra (Indonesia). The total EOR cost includes the costs for capture (based on 3% CO<sub>2</sub> stream), concentration, transport, and injection. Possible oil revenues from these EOR injections are not included here, but they would make CO<sub>2</sub> utilisation via EOR more attractive. Preliminary assessment showed that among the three sites studied, EOR at South Sumatra would be most economical due to the shortest distance.

**Table 3.14: CO<sub>2</sub> Mitigation and cost of EOR for Singapore in regional areas**

Reservoir	Distance from Singapore (km)	CO <sub>2</sub> Reduction		EOR Cost
		Amount (mtpa)	%	(\$/t)
Sarawak, Malaysia	1029	0.29	0.64	236.7
East Kalimantan, Indonesia	1401	0.77	1.69	259.1
South Sumatra, Indonesia	470	0.40	0.80	203.2

Detailed studies of possible EOR/storage sites around Singapore, including geographical limitations, distances, and economical feasibility, would be necessary in order to make a more informed decision regarding the feasibility and appropriateness of EOR for Singapore. Furthermore, although EOR has been practiced for nearly 40 years, it was not intended for

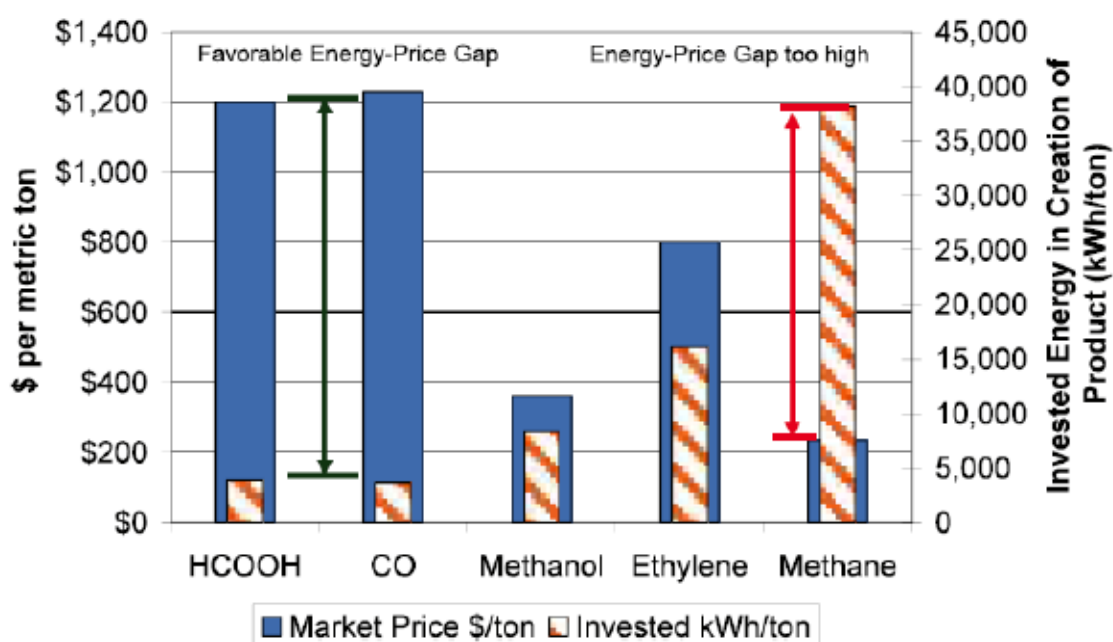
<sup>24</sup> Refer to natural occurring gases that expand in a reservoir which is then used for EOR. Until recently, most of the CO<sub>2</sub> used for EOR came from natural occurring reservoirs.

<sup>25</sup> Refers to gases emitted from human activities (such as combustion of fossil fuels)

CO<sub>2</sub> mitigation. In reality, only a fraction of the injected CO<sub>2</sub> remains in the reservoir. Thus, detailed lifecycle analysis, and several operational and monitoring elements in the EOR process is required to determine the net removal of CO<sub>2</sub> emissions.

### 3.3.2.5 Electrochemical Utilisation

CO<sub>2</sub> can be reduced electrochemically to several products including formic acid (HCOOH), carbon monoxide (CO), methanol, ethylene and methane etc. Figure 3.10 illustrates the price-energy differentials for the electrochemical production of these chemicals from CO<sub>2</sub>.



**Figure 3.10:** Market prices and energy requirements for the production of various chemicals via electrochemical conversion of CO<sub>2</sub>

Despite their approximately similar price-energy differentials (seen in Figure 3.10), formate/formic acid (HCOOH) production has received more attention than carbon monoxide CO. This is due to the difficulty in storing and transporting CO. In the following sections, the economics and impact of converting CO<sub>2</sub> to formic acid via electrochemical process are discussed. There are 2 main methods used for the electrochemical production of formic acid:

- Method A: Utilising a consumable chemical (e.g. NaOH) at the anode
- Method B: Utilising wastewater at the anode and recycling of any consumable chemicals



Table 3.15 shows the difference between the energy consumption and net CO<sub>2</sub> emissions from the two methods. It can be seen that electrochemical conversion of CO<sub>2</sub> to formic acid increases the overall CO<sub>2</sub> emissions, making this utilisation method undesirable and unsuitable from the point of view of CO<sub>2</sub> mitigation.

**Table 3.15: Difference between Method A & B of producing formic acid from electrochemical utilisation**

Method	Energy consumption (kWh/tonne formic acid)	Formic acid production (MT/year)	Net CO <sub>2</sub> emissions (MT/year)
Method A	7,111	39.1	105
Method B	8,642	39.1	136

### 3.3.3 Economics of Utilisation in Singapore

Estimating the cost for non-EOR CCU is much more complex as compared to CCS as it is dependent on a variety of additional options, feedstocks, reactions, processes and products. For example, CCU using solar based hydrogen would incur a much higher cost than one involving natural gas based hydrogen. Furthermore, most of the CCU processes and reactions are in early R&D, so it is difficult to estimate the energy requirements and costs.

Nonetheless, it is evident from the literature that the cost incurred for CCU will be higher as compared to CCS. However, due to the limited space for sequestration and the unknown hazards associated with the sequestered CO<sub>2</sub>, utilisation options may need to be explored in Singapore. Further research would be required to make utilisation options more efficient and economical so as to be a more attractive option for carbon mitigation.

## 4. CONCLUSION AND RECOMMENDATIONS

### 4.1 KEY FINDINGS

- Carbon capture and storage/utilisation (CCS/U) from major stationary sources is a potential technology which can help reduce carbon emissions. However, challenges such as achieving cost-effectiveness and low energy penalties for CCS/U and finding demand for carbon utilisation products have to be overcome.
- Among the three modes of capture, namely pre, oxy, and post, pre-combustion technology based on natural gas offers the least energy penalty for carbon capture.
- For Singapore, CO<sub>2</sub> utilisation assumes greater importance for longer-term CO<sub>2</sub> mitigation due to geological constraints. However, cost estimates must be refined further through detailed modelling of the various chemical routes step-wise through the unit operations.
- The quantity of some products (e.g. formic acid, acetic acid and formaldehyde) from the carbon utilisation of Singapore CO<sub>2</sub> emissions alone far exceeds current global demand for them. Therefore, the most practical means of CO<sub>2</sub> utilisation is to produce liquid fuels such as methanol, ethanol, and hydrocarbons, and mineralisation products for landfill and the construction industry.
- Solar hydrogen is a crucial reactant for CO<sub>2</sub> utilisation in liquid fuel production or the production of the C<sub>1</sub> – C<sub>4</sub> chemicals mentioned earlier, but its production entails trade-offs against using solar PV for electricity generation.
- CO<sub>2</sub> utilisation via micro-algae in Singapore context is limited by the availability of resources, such as land, water and the photosynthetic yields. The impact on CO<sub>2</sub> reduction may not be significant, but opportunities exist for the production of high-value added, niche products such as pharmaceuticals, nutraceuticals, and feeds for agriculture and aquaculture applications.
- Electrochemical conversion of CO<sub>2</sub> to formic acid does not look favourable from a carbon mitigation perspective. Its energy requirements result in increases rather than decreases in CO<sub>2</sub> emissions.
- The traditional material-centric R&D approach alone will be unable to address the CCS/U challenges. Holistic systems analysis and process chemistries and engineering are vital. It is necessary to look at CCS/U options using a system-centric approach.

## 4.2 KEY RECOMMENDATIONS

Major recommendations including R&D directions are grouped in the following four sections: (1) Overall, (2) Capture and Concentration, (3) Storage and Sequestration and (4) Utilisation.

### Overall

- Both capture and utilisation of CO<sub>2</sub> for producing fuels, chemicals, and products will require sustained long-term research to develop appropriate, economically viable technology options based on novel solutions and insights.
- The traditional material-centric R&D approach alone will be unable to address the challenges of CCS/U. Proper integration of material, process, and system considerations and fruitful interaction across disciplines will be critical. This will require a paradigm shift in the future R&D directions.
- The material and technology research needs related to CCS/U must be evaluated based on their performance in the context of the overall process/system. This overall system-level performance includes economic viability (CAPEX and OPEX), use of green feedstocks, and minimisation of energy penalty and plant footprints. Hence, these should form an integral part for evaluating all future R&D in CCS/U.

### Capture and Concentration

- Low CO<sub>2</sub> concentrations in Singapore's emissions are largely due to the predominant use of natural gas for power/energy, unlike in other large countries.
- Oxy-combustion and post-combustion are the two options for CCC from existing power plants. Research leading to any improvement in air separation efficiency will be beneficial. Pre-combustion option is preferred for greenfield power plant developments.

### Storage and Sequestration

- R&D for the long-range cost-effective transport (supply chain and logistics) of concentrated CO<sub>2</sub> to Asia Pacific regional sites will be essential for exploiting the CCS option, which is viewed globally as a short-term solution. Even if technological solutions are available, political and economic considerations must also be taken into account in exploring potential CCS options.

## Utilisation

- In the CCS/U literature, Enhanced Oil Recovery (EOR) and Enhanced Coal Bed Methane Recovery (ECBMR) are viewed as utilisation options. These may become viable for Singapore with cooperation from neighbours in the region.
- Utilisation options via innovative organic, inorganic, or biological reactions to convert CO<sub>2</sub> into useful products can also enhance Singapore's energy resilience. However, only liquid fuels such as methanol, ethanol, and hydrocarbons, and mineralisation products for the building and construction industry can make a dent in CO<sub>2</sub> emission reduction. Although these CCU options may still result in CO<sub>2</sub> emissions if non-renewable fuels are used in the utilization process, there would still be a net reduction in CO<sub>2</sub> emissions especially for the lower energy intensive CCU options such as mineralization. The economics of these CO<sub>2</sub> products are still not favourable, and require much more R&D effort, support, and detailed life cycle analysis.
- Efficient activation of CO<sub>2</sub> will require high-energy, renewable reactants (such as solar hydrogen), novel catalysts, processes, and systems.
- Micro-algae research should focus on genetic modifications to enhance productivity of targeted high-value added niche products, and process development in order to optimise resource usage.

## 5. APPENDICES

### APPENDIX A

#### Minimum capture energy and cost of CC

Assuming that all separations take place at room temperature, the minimum work ( $E_{min}$ ) required for capturing CO<sub>2</sub> from the above sources is given in Table A.1. The CO<sub>2</sub> concentrations in the respective streams are also included in Table A.1. Practically achievable targets for these capture energies ( $E_{target}$ ) are assumed to be 5X the thermodynamic limits. Capture cost is computed assuming that  $E_{target}$  will be supplied as electricity.

**Table A.1: Minimum and target energies required for CO<sub>2</sub> capture from various sources**

Capture Stream or Emission Source (mol% CO <sub>2</sub> )	$E_{min}$ (MJ/tonne CO <sub>2</sub> )	$E_{target} = 5E_{min}$ (kWh/tonne CO <sub>2</sub> )	Capture Cost (\$/tonne CO <sub>2</sub> )	Capture Type
Refineries and power plants using natural gas (3%)	252.9	351.3	79.0	Post
Power plants using fuel oil (8%)	196.2	272.5	61.3	Post
Coal-fired power plants (15%)	158.7	220.4	49.5	Post
Exhaust stream from FCC in a refinery (20%)	140.9	195.7	44.0	Post
Power plants using natural gas reforming (25%)	126.7	175.9	39.6	Pre
Power plants using fuel oil gasification (33%)	108.2	150.3	33.8	Pre
Power Plants using coal gasification (40%)	94.7	131.6	29.6	Pre
$E_{target} = E_{min} \times 5/0.0036$ Capture cost = $E_{target} \times$ Price of electricity (\$ 0.2248/kWh) Reference: 1 \$ = 0.80 US\$ (2012) Unless otherwise mentioned, flue gas pressures is assumed to be at atmospheric pressure and about 40 - 50°C				

**Calculations of CCS Cost**

In order to compute the target cost for **post-combustion CCS** from Singapore's emissions, calculations were made with assumptions such as transport via pipelines to sequestration sites, compression at the storage sites, and storage or injection and others. It is assumed that the amortised capital expenditure over 15 years for a CCS/U process is some fraction of its annual operating expenditure exclusive of raw material costs. The cost equation is as follows:

$$CCS\ Cost\ \left(\frac{\$}{tonne}\right) = OPEX(1 + x) + \$7 + \$9 = \$16 + (1 + x)(capture\ cost + \$27)$$

**Assumptions**

- Compression pressure = 120 bar
- Captured and concentrated CO<sub>2</sub> is 98.0 vol% with 2 vol% N<sub>2</sub> at 1 bar
- OPEX = Capture Cost (Appendix A) + Pressurising Cost; where pressurising cost = \$27/tonne CO<sub>2</sub><sup>26</sup>
- CAPEX =  $x$  X OPEX, where  $x$  is an assumed ratio of CAPEX to OPEX cost.
- Pipeline CO<sub>2</sub> transport = \$7/tonne CO<sub>2</sub> for onsite sequestration. Cost of transport to regional sites requires additional cost of \$0.06/tonne/km.
- Storage cost = \$9/tonne CO<sub>2</sub>
- CCS cost to decrease by 2.5%/year from 2015

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<sup>26</sup> Based on a simulation model in Aspen Hysys, using the Peng-Robinson equation of state, adiabatic compression with an efficiency of 0.75, final pressure of 120 bar, and current electricity price in Singapore of 0.2248 \$/kWh. The energy required for compression is 123 kWh/tonne.

**Calculations of CO<sub>2</sub> Avoided from the Production of Biofuels**

The net emissions mitigated from the production of biodiesel, bioethanol and biomethane is calculated via the following equation and assumptions

$$\begin{aligned} \text{Net CO}_2 \text{ avoided} &= \text{CO}_2 \text{ consumed by microalgae} + \text{Emissions avoided} \\ &- \text{Emissions}[\text{Algal bioreactor} + \text{Algal process} + \text{Biofuel use}] \end{aligned}$$

**Assumptions:**

- 10% of Singapore area (710 km<sup>2</sup>), which may comprise onshore and offshore facilities, is available for the cultivation and processing of microalgae.
- Rate of algal growth = 20 g dry biomass/m<sup>2</sup>/day<sup>27</sup>
- CO<sub>2</sub> consumption rate = 1.8 kg CO<sub>2</sub>/kg dry biomass
- Yield = 0.17 g/g dry biomass (biodiesel)
- Yield = 0.21 g/g dry biomass (bioethanol)
- Yield = 0.18 g/g dry biomass (biomethane)
- Energy yield equivalent units:
  - 1 L bioethanol = 0.67 L gasoline
  - 1 L biodiesel = 0.98L diesel
  - 1 L biomethane = 0.93 L natural gas
- Energy consumption for algal bioreactors = 4.16 kWh/kg dry biomass
- Energy consumption for algal processing = 0.73 kWh/kg dry biomass

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<sup>27</sup> Based on growth of microalgae using the flue gas from a natural gas fired power plant.

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## Lead Agencies



## Commissioning Agencies

