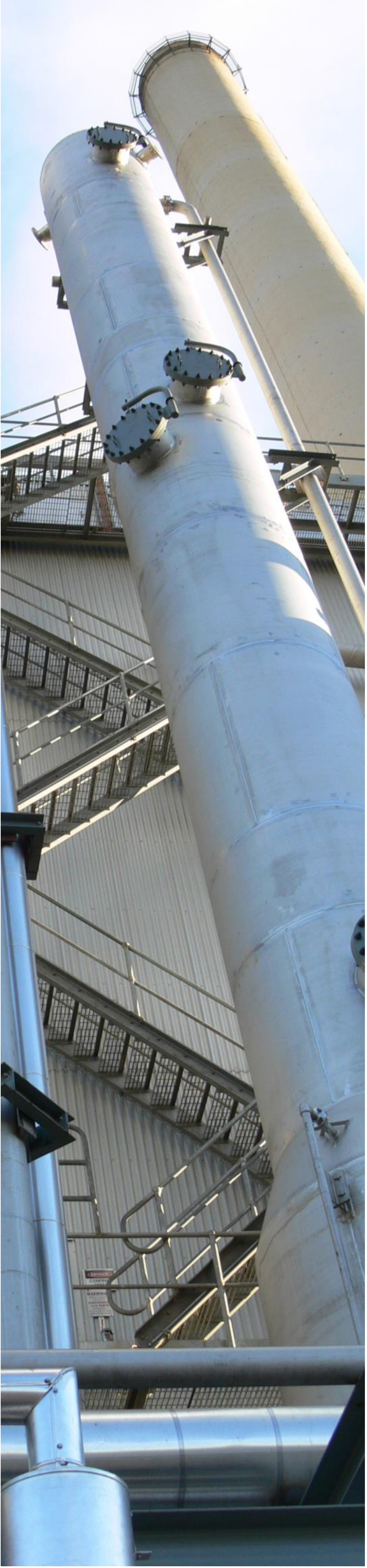

AUSTRALIAN CARBON INNOVATION

OPPORTUNITIES FOR CARBON DIOXIDE RECYCLE IN VICTORIA

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GLOSSARY OF TERMS

BPA	Bisphenol A
BPA-PC	Bisphenol A polycarbonate
CCS	Carbon capture and storage
CCUS	Carbon capture, utilisation and storage
CO	Carbon monoxide
CO_2	Carbon dioxide
CRI	Carbon Recycling International
DAC	Direct air capture
DMC	Dimethyl carbonate
DME	Dimethyl ether
DMM	Dimethoxymethane
DPC	Diphenyl carbonate
EC	Ethylene carbonate
EDBM	Bipolar membrane electrodialysis
EOR	Enhanced oil recovery
FTS	Fischer-Tropsch synthesis
GC	Glycerol carbonate
GHG	Greenhouse gas
HESC	Hydrogen Energy Supply Chain
IPCC	International Panel on Climate Change
NIPU	Non-isocyanate polyurethane
PC	Propylene carbonate
PCC	Precipitated calcium carbonate
PEM	Polymer-electrolyte membrane
PHB	Poly(3-hydroxybutyrate)
PHU	Poly(hydro urethane)
PPC	Polypropylene carbonate
R&D	Research and Development
REE	Rare earth element
RWGS	Reverse water-gas shift
SCFX	Supercritical fluid extrusion
S-CO_2	Supercritical carbon dioxide
SMR	Steam methane reforming
SNG	Synthetic natural gas
SOE	Solid oxide electrolysis
Syngas	Synthesis gas (predominantly carbon monoxide and hydrogen)
TRL	Technology Readiness Level

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1 Executive Summary

CO_2 recycling is the process of turning captured CO_2 waste into value-added products that keep the CO_2 out of the atmosphere and create revenue. The development of CO_2 recycling technologies, and successful businesses based upon them, is essential to effectively address the collective challenge presented by rapid global warming. To limit global warming to 1.5 ^{o}C, the IEA warns that CO_2 must be extracted from the atmosphere as a matter of urgency, but the quantities required will require a gargantuan effort over the next 50 years and longer. A global shift of emphasis toward net-negative emissions is needed, which requires large-scale capture of atmospheric CO_2 and permanent storage of the CO_2 either underground or in manufactured products.

This report provides an overview of the five different classes of CO_2 recycling process, including the companies that are championing their commercial development of their processes, any relevant research work currently under way in Victoria, and ACI commentary on their readiness for commercialisation, and the opportunities they present for Victoria. The main findings are summarised in Section 4, which outlines the most prospective pathways for commercialisation of CO_2 recycling in Victoria.

This report finds that Victoria is very well placed to take a leading role in addressing the global warming challenge. While the Victorian Government currently has policies to stimulate deployment of clean energy technologies, it is unlikely that they will be sufficient to meet the 1.5 ^{o}C target in and of themselves. It is probable that large-scale CO_2 capture and recycling will be required for local production of clean (green and blue) hydrogen by gasification of fast-growing biomass crops and lignite, coupled with the vast CO_2 storage capacity in the Gippsland Basin, and by the introduction of CO_2 capture and recycling in industrial processes. The cost of CO_2 capture can be offset through production of 'green' concrete, fertilisers and industrial chemicals, reducing the carbon footprint of high-carbon imported products and creating new industries and employment in the State.

This report identifies thirteen technologies that have potential to make significant and meaningful contributions to Victoria's economic growth and emissions reduction efforts. The selected technologies, listed in the following table, range from 'fully commercial' to 'needs more work', with projected commercialisation timeframes in the short-, medium-, and long-terms. The rationale for selection of these technologies is briefly explained, with more details provided in Section 4.1.2.

Summary of identified opportunities for CO_2 recycling in Victoria

CO_2 Recycling Technology	**Product Opportunities Arising**	**Developmental Status**	**Rationale for Selection**
Urea	Import replacement of a major fertiliser used in Australian agriculture.	Commercial and gasification tested by 2 commercial vendors.	Actively being actively investigated for commercialisation in Victoria.
Carbonation of concrete	Reduced emission intensity of concrete in construction and infrastructure projects.	Commercial and now available in Australia.	CO_2 alone gives an immediate reduction in a major industry sector. Potential to double the reduction using baking soda. Potential to incorporate DAC or biogenic CO_2 for greater emissions reduction.
Glasshouse horticulture	Reduced use of CO_2 produced by natural gas combustion in glasshouse production of tomatoes, herbs, flowers, pharmaceutical cannabis, etc.	Already used commercially in some places overseas, but not yet widespread in Australia.	Immediate boost to an existing horticulture industry in the Latrobe Valley. Many product opportunities. Potential for domestic and/or export markets. Opportunities for value-adding using S-CO_2. Biomass waste can be gasified to green hydrogen.
Supercritical CO_2 processing (S-CO_2)	Solvent-free extraction of oils and de-fatting of seed proteins for food ingredients; water-free textile dyeing.	A small food ingredients company in Tasmania, but otherwise not yet commercialised in Australia.	New business opportunity in water-free textile dyeing. Potential for opportunities in defatting of hemp seeds, fruit/vegetable powders, natural colours and flavours, edible and pharmaceutical oils, bioingredient extracts (e.g., hop, pharmaceutical cannabinoids).
Bipolar membrane electrodialysis (EDBM)	Production of acids and alkalis from simple salts using renewable energy, producing alkali for use in CO_2 capture, production of sodium bicarbonate, etc.	Commercially available, used in water industry.	Versatile technology, enabler of new opportunities, compatible with renewable energy. Produces NaOH for production of baking soda, carbonation of fly ash, and DAC.
Carbonated fly ash	Transformation of a hazardous waste into aggregate for ‘green’ concrete.	Commercialised overseas, but hindered by prescriptive building standards.	Simple chemistry. Ideal way to monetise the massive amount of heritage

			waste fly ash in the Latrobe Valley. Potential for a variety of low-emissions concretes and building materials for the construction industry. Links to Ca/Mg carbonate and DAC.
Ca/Mg carbonate	Additive for ‘green’ concrete and plasterboard.	Commercialised overseas, and being investigated by Mineral Carbonation International in NSW.	Synergistic with baking soda production. Direct link to DAC, and route to adding value to DAC.
Syngas by SOE	High efficiency production of syngas using renewable energy, key enabler for many other products.	Under development by CSIRO and collaborators.	Syngas a versatile industrial chemical feedstock. SOE is more economical at small scale than gasification. Scale appropriate for biological conversion to ethanol or edible biomass.
Methanol	Important chemical industry feedstock.	Commercial overseas, but more expensive than conventional product. Research needed for more efficient catalyst.	A major industrial chemical feedstock. Research interest/expertise in Victoria to build upon.
Ethanol	Important biofuel and precursor to ethylene, a major industrial feedstock.	Early-stage R&D overseas, but poised to take off.	‘Green’ polyethylene could be produced in Victoria, to make non-biodegradable, recyclable plastics.
Ethylene carbonate	Important ‘green’ chemical industry feedstock and solvent in lithium-ion batteries.	Improved catalyst and reactor design for renewable feedstock being researched at Monash University.	Potential for domestic production of ‘green’ solvent for lithium-ion batteries. Research interest/expertise in Victoria to build upon.
Lignin-based polurethane	Versatile route to plant-based plastics, rubbers and adhesives.	Early-stage exploratory.	Potential to add value to lignin waste from Latrobe Valley papermaking plant.
Hydrogen-oxidising bacteria	Proteins for human and animal food.	Engineering R&D required to scale up a potentially explosive gas fermentation.	Potential for production of edible biomass/protein for aquafeed and human food products. Alternative to using biological conversion of syngas.

The anticipated timeframe for commercialisation of each technology is shown below. The technologies listed as ‘short-term’ have been commercialised overseas and could form the basis of new businesses in Victoria.

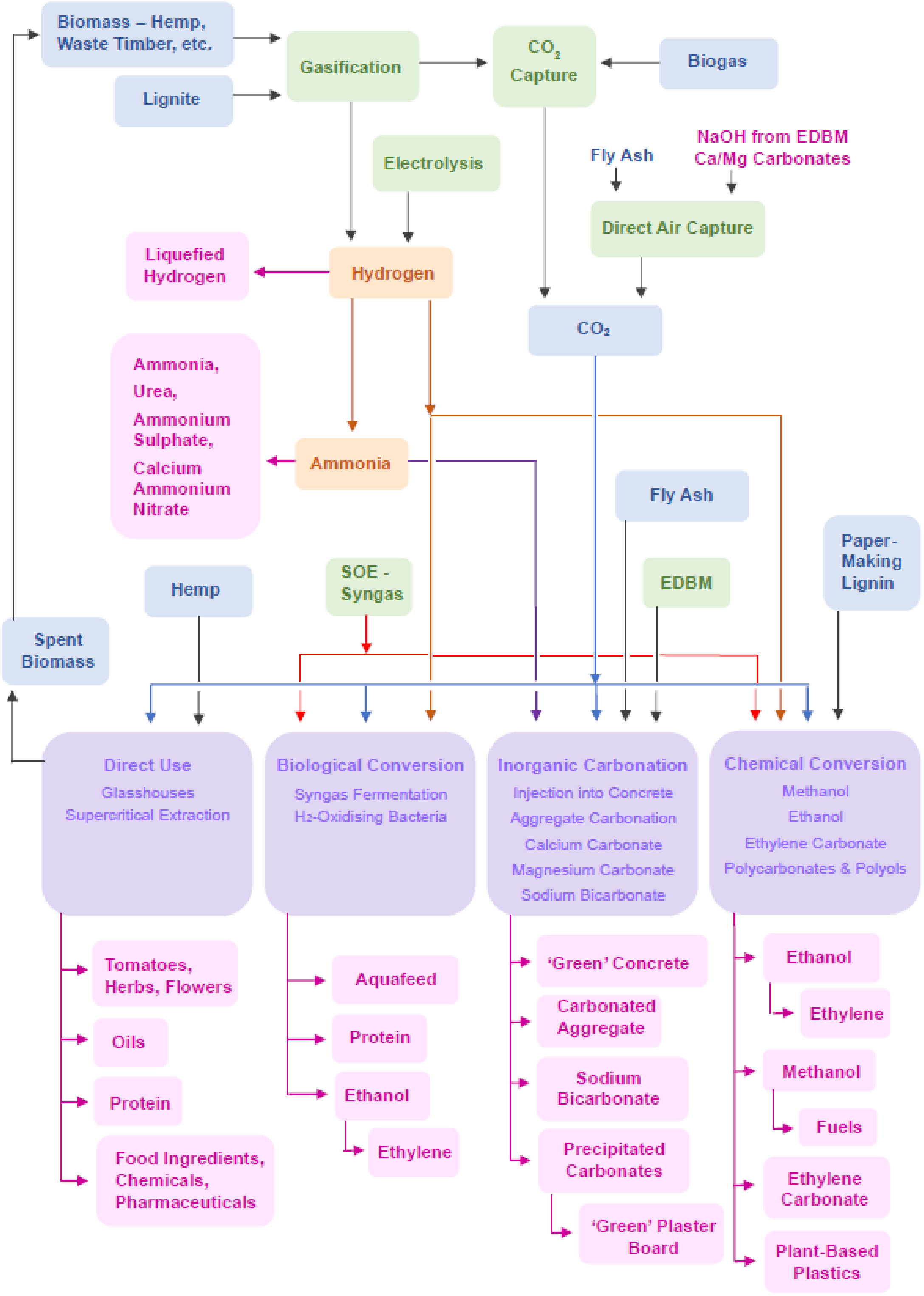
	SHORT-TERM	INTERMEDIATE	LONG-TERM
TRL 1-3			Ethanol Ethylene Carbonate Lignin-based Polyurethane H_2-oxidising bacteria
TRL 4-6		Carbonated Fly Ash Ca/Mg Carbonates Methanol Syngas by SOE EDBM	
TRL 7-9	Concrete Carbonation Glasshouse Horticulture S-CO_2 Processing	Urea	

Timeframe for commercialisation of prospective CO_2 recycling opportunities

This portfolio of technologies includes a mixture of technologies that are mostly at commercial or pilot scale, with some requiring fundamental research to develop their potential. The short-term opportunities represent the least complicated uses for CO_2, while the other options require active research to develop their potential. Commercial equipment is available for urea production, but this has a longer timeframe than the direct uses of CO_2. This is due to the requirement to have an active gasification process in place to produce hydrogen, then to produce ammonia and then urea. There are no active plans for this to occur, other than a speculative proposal by Victorian Hydrogen & Ammonia Industries Ltd (VHI), so the timeframe for ammonia production is beyond what would be considered ‘short term’.

This portfolio of technologies was selected because it has the potential to create and support an ecosystem of interdependent new industries in the Latrobe Valley, a green technology hub, making use of the resources that could conceivably become available over time. Fortunately, an existing research skills base is available in Victoria to support this technology development pathway for CO_2 recycling, and work is already occurring on some of the nominated technologies. The illustration on the following page shows the types of connections that could be made, and the range of products that could be produced, in a green technology hub in the Latrobe Valley.

It is assumed that low-emissions hydrogen and/or ammonia will be commercialised in the Latrobe Valley in the not-too-distant future, and that there is an abundant supply of CO_2 that can be tapped off from a transport pipeline for recycling. It is also assumed that barriers to remediation of the massive stockpiles of power station fly ash are successfully overcome. Local sources of renewable energy (wind, solar, geothermal) will be used for electricity and heat, and strategically-planted crops of plantation timber and/or industrial hemp are an available source of biomass. Both direct air capture (DAC) and biogas produce carbon-neutral CO_2 for upgrading.



Identified prospective opportunities for CO_2 recycling in Victoria

This overview picture is based on recommendations made by ACI throughout this report, which can be found collated in Section 4.1.6. The identified CO_2 recycling opportunities are broadly aligned with the findings of previous reviewers, including CSIRO's *'CO_2 Utilisation* Roadmap', while also reflecting the unique resources available in Victoria; in terms of natural resources, commercial interests, and existing research activities.

A key finding of this report is that a variety of technologies for inorganic carbonation have already passed through the R&D phase and been successfully commercialised overseas. CarbonCure has standardised its system for injection of CO_2 into concrete slurry and sold more than 650 units in thirty countries, producing about 5 million truckloads of low-carbon concrete. Systems for producing low-carbon concrete blocks, slabs, pavers and tiles have been commercialised by Solidia, Carbicrete, CarbonBuilt. Carbon8 Systems has commercialised its process for direct carbonation of solid wastes, and Blue Planet has commercialised its process for continuous extraction of Ca/Mg from solids and precipitation as Ca/Mg carbonates. CarbonFree has commercialised its process for producing baking soda using hydroxide extracted from low-cost salts.

This is significant, because these represent high-volume low-value markets that can achieve significant CO_2 emission reductions, mostly for the construction sector, including concrete formwork, pre-formed concrete blocks, slabs, etc., insulation and plasterboard. This is an ideal way to foster a low-emissions economy, because the captured CO_2 is permanently sequestered into valuable products in a sector that is large and continually growing.

As such, inorganic carbonation is an area of R&D that urgently needs to be kick-started in Australia. Coordinated research by both industry and academia is required, supported by policy direction from the government. The scale of the opportunity is significant, with Victoria using around 16 million tonnes of cementitious product each year. Reducing the associated GHG emissions, and preferably reaching net-negative, is essential for the state to meet its net zero by 2045 target.

Victoria is well placed to capitalise on this opportunity. The power stations in the Latrobe Valley have produced tens of millions of tonnes of Ca/Mg-rich fly ash, which could be upgraded by carbonation into a supplementary cementitious material, creating a new revenue stream for the power companies. The fly ash could be further value-added by solubilising the Ca/Mg components for reaction with CO_2 or sodium bicarbonate, with possible separation of the Ca and Mg components, to produce Ca, Mg or Ca/Mg carbonates as individual products.

The CarbonCure CO_2 injection system is a short-term opportunity that is now available in Victoria through BOC Gases. This technology is commercially available and easily deployable, and has the potential to make a significant contribution to reducing greenhouse gas emissions in Victoria if widely deployed in the construction industry and Government infrastructure projects. Injection of captured CO_2 into fresh concrete has the potential to reduce the State's consumption of cement by about 1.3 Mt and eliminating 1 Mt of CO_2 emissions, equivalent to taking 11%, or ~350,000, cars off Victoria's roads.

ACI recommends that policymakers assess whether there are any barriers, e.g., building standards, that would preclude the deployment of CarbonCure technology in Victoria. If not, then this should become part of standard practice and mandated for all new infrastructure projects. If barriers are identified, then Government-sanctioned trials should be undertaken to validate this process for inclusion in the relevant codes and standards. The Victorian Government could also provide essential support through public procurement of low-carbon products with verifiable climate benefits, and incentives for the public and private sectors to invest in and consume these products. The “Big Build” initiative is a once-in-a-generation opportunity to demonstrate innovation in the materials procurement process for Victoria.

This study has also identified, for the first time, that three water treatments plants in the Melbourne metropolitan area (Western, Eastern and Yarra Valley) collectively produce about 100,000 t/y CO_2 which, if captured and stored, would qualify as carbon-negative emissions. CO_2 capture systems suited to this scale of operation are commercially available, prefabricated for easy installation (Section 5.1.2.2). Injection of this biogenic CO_2 into concrete would significantly help the construction sector reduce its greenhouse gas emissions. **ACI recommends that a study be undertaken to investigate the issues and likely costs involved in implanting CO_2 capture at municipal water plants, identify any policy barriers that need to be addressed, and identify or suggest possible incentives that could assist in bringing this to reality.**

Also, Boral’s Blue Circle Southern cement works in Waurn Ponds produces cement kiln dust as a by-product. Modular CO_2 capture systems could also be used to capture CO_2 emissions from the kiln flue gas for carbonation of the kiln dust. This combination would make the cement from Blue Circle Southern close to carbon neutral. **ACI recommends that this option be included in the above recommended study.**

The second short-term opportunity identified in this study, use of CO_2 in glasshouse horticulture, represents a potential customer for CO_2 captured from water treatment biogas. There are existing glasshouse horticulture businesses in Victoria which rely on gas burners to generate CO_2, and require alternatives to help transition away from natural gas use. Overseas, CO_2 from biogas is trucked or piped to glasshouse horticulture facilities. In principle, there is no reason why this could not be done in Victoria. **ACI recommends that a study be undertaken to engage with Victorian glasshouse horticulturalists and investigate the potential business case for using captured biogenic CO_2 to enhance crop production while reducing the emissions intensity of glasshouse horticulture.**

The third short-term opportunity identified in this study, supercritical CO_2 (S-CO_2) processing (Section 3.1), is commercially available technology but has no local business uptake. This is an instance where a pilot-scale development facility would encourage local entrepreneurship and development of new business opportunities. Federation University in Churchill would be an ideal location for such a facility, to encourage monetisation of existing and new plant crops, and production of new food and pharmaceutical ingredients. **ACI recommends that a business plan be developed for a S-CO_2 R&D facility located at Federation University.**

Production of urea is listed as an intermediate-term opportunity in Victoria, even though it is an established commercial process. This is because it is secondary technology, being dependent on commercial availability of sufficient quantities of hydrogen (green or blue) and CO_2 (fossil or biogenic).

Over time, increasing demand from Japan for hydrogen and ammonia as clean fuels will stimulate investment in both hydrogen and ammonia production in Victoria, predominantly from lignite but supplemented by renewable energy and biomass. Establishment of these capabilities is likely to be a necessary precursor for urea production in Victoria. As is done elsewhere, the balance of production could be shifted between ammonia and urea in response to market demand and relative prices, to maximise profitability. **ACI recommends continued development of skills in industrial pilot scale gasification of lignite and biomass, and the associated skills in CO_2 capture and processing and hydrogen processing.**

The other opportunities placed in the intermediate-term category (carbonated fly ash, calcium/magnesium carbonates, methanol, syngas by SOE, EDBM) are not yet ready for commercialisation in Victoria. In some cases, appropriate technologies have been developed overseas and could potentially be utilised in Victoria, e.g., Carbon8 Systems, Blue Planet, or could be adapted from other industries, e.g., EDBM. Some are being investigated by local researchers. However, in the absence of support from government and the community, these opportunities will not materialise.

The opportunities placed in the long-term category (ethanol, ethylene carbonate, lignin-based polyurethane, H_2-oxidising bacteria) are seen as having potential to be the basis for new manufacturing industries in Victoria, including green fuels, plastics and food ingredients. These require further research at lab scale and then scale-up, and currently lack any industrial support. Research is also required on development of compact solar thermal heat storage systems, to provide the high temperatures (~600 ^{o}C) needed to overcome the energy barrier of CO_2 conversion. **ACI recommends that government funding be allocated to support strategic research to underpin the creation of these new manufacturing industries in Victoria.**

Beyond this, there are likely to be opportunities for conversion of CO_2 into high-value low-volume fine chemicals (e.g., acetic acid, benzoic acid, acrylic acid, carbonic acids, esters and lactones), all of which are precursors to many industrial products, but these are beyond the scope of this report. **ACI recommends that an independent review of developments in this area be undertaken by a qualified expert, to provide guidance on the opportunities that exist for strategic research efforts.** This review should include detailed consultations with representatives of the relevant chemicals and plastics industries.

Given the urgency with which the climate change emergency must be addressed, new thinking is required on how to stimulate and support the development, demonstration and commercialisation of new CO_2 capture and recycle technologies in Australia. In the absence of any kind of pricing mechanism that reflects the value to society of CO_2 capture and recycle, market forces alone will not deliver the necessary outcomes.

Previous reviews have shown this to be a global challenge. It is broadly understood that CO_2 recycling technologies can only be successfully introduced if they are seen as desirable and are actively supported and coordinated at all levels – policy, industry and public. To this end, it is worth repeating the **key recommendations made by previous reviewers** (Section 3.1):

- Awareness of CO_2 recycling and its role in the decarbonisation challenge needs to be raised within government, the private sector and the wider public.
- At the same time, public awareness needs to be raised of the life cycle emissions associated with existing fossil-based products, highlighting the changes that individuals can bring about through their collective choices.
- Early opportunities, such as the use of CO_2 in building materials, can be stimulated through Government support for product testing trials and updating of standards, and through public procurement of low-carbon products with verifiable climate benefits, further supported by incentives for the public and private sectors to invest in and consume these products.
- Financial incentives and mechanisms are needed to accelerate investment in CO_2 recycling technology research and development, as well as demonstration at the scale needed to attract further investment.
- Support mechanisms are needed that allow CO_2 recycling to receive recognition for sustainability benefits and compete on a more level-playing field with conventional products, including integration with existing strategies and green mechanisms.
- A piecemeal approach will not be successful. Engagement and close collaboration between all interested parties is required, and knowledge transfer must be facilitated.

An additional issue faced by technology developers in Australia is that there are insufficient support mechanisms to help bridge the “chasm of death” between laboratory research and pre-commercial demonstration. A new approach is needed. Following the successful example of the NRG COSIA Carbon XPRIZE in the U.S., which brought together technology developers with large industry and private philanthropists, it is suggested that a similar competition could be run in Victoria to actively encourage the commercial deployment of CO_2 recycling in the Latrobe Valley. This would kick-start the scale-up of promising new technologies and draw established technologies to Victoria, create new businesses and jobs, and lay the foundation for a green industrial ecosystem in the Latrobe Valley.

ACI recommends that a scoping study be undertaken to investigate how a competition of this nature might be set up and run in Victoria. A working group of interested parties should be established to oversee this process, including representatives of relevant State government departments, to ensure that any regulatory hurdles are identified and addressed.

Finally, it is worth emphasising that successful production of value-added products from CO_2 is dependent on the availability of clean energy and green/blue hydrogen. As supporting infrastructure, **ACI recommends that the following areas of technology development should also be prioritised:**

- Development of compact **solar thermal heat storage** systems, to provide the high temperatures (~600 ^{o}C) needed to overcome the energy barrier of CO_2 conversion.

- Continued development of skills in **industrial pilot scale gasification of lignite and biomass, and the associated skills in CO_2 capture and processing and hydrogen processing**. These skills are also needed to underpin Victoria’s future hydrogen export industry.

The thirteen technologies identified by ACI in this report have potential to make significant and meaningful contributions to Victoria's economic growth and emissions reduction efforts. This portfolio was selected because it has the potential to create and support an ecosystem of interdependent new industries in the Latrobe Valley, a green technology hub, making use of the resources that could conceivably become available over time, i.e., renewable energy, green-blue hydrogen and ammonia, CO_2 transport pipeline, fly ash, sustainable biomass, DAC and biogas. These can be transformed into the essential elements of a net-negative green economy: foods and pharmaceuticals, low-emissions construction materials, fertilisers, valuable industrial chemicals and plant-and-CO_2-based recyclable plastics.

CO_2 recycling should thus be seen as a key enabling technology, or suite of technologies, that can underpin new industries and employment in the State and make significant, meaningful contribution to reducing the State's greenhouse gas emissions. Victoria is very well placed to take a leading role in addressing the global warming challenge through the deployment of CO_2 recycling technologies, but it requires the active support and facilitation of the State Government to remove regulatory barriers and stimulate engagement by industry and the public.

2 What is CO_2 Recycling, and Why?

2.1 INTRODUCTION

Carbon dioxide (CO_2) is an odourless and colourless gas that is the end product of any combustion process, either biological or chemical, and represents a "spent" form of carbon. It is a potent greenhouse gas that is accumulating to dangerous levels in the atmosphere and oceans, primarily through human activities which release in the order of 37 billion tonnes of CO_2 each year.[1]

This rate of CO_2 accumulation in the atmosphere is unprecedented, and international emissions reduction targets are insufficient to prevent potentially catastrophic global warming. At this stage, 2023 looks set to be the hottest year in 125,000 years.[2] Global warming is expected to exceed 1.5°C in the 2020s and 2°C before 2050 (Hansen et al. 2023), and >3°C by 2100 (DeConto et al. 2021). The Department of Energy, Environment and Climate Action estimates the cost of damage from climate change in Victoria will be over $150 billion by 2050, escalating to about $1 trillion by 2100. It estimates that every $1 spent on adapting to climate change now saves society an average of $6 in future costs. Victoria cannot afford to delay action.[3]

In order to lower the risk of a global climate catastrophe, it is necessary to accept the reality of global warming as an existential threat to humanity, and make every possible effort to limit global temperature rise to no more than 1.5 °C. It is no longer possible to think that this can be done by shutting down fossil fuel power stations and introducing renewable energy. That should have been done globally at least 10 years ago but the opportunity was not exploited. From now on, it will be essential to actively withdraw CO_2 from the atmosphere, in staggeringly large quantities.

The IEA suggests that it will be necessary to scale up CO_2 removal from the atmosphere, through 'bioenergy equipped with CCUS' (BECCS) and 'direct air capture and storage' (DACS), to over 5 Gt/y CO_2 during the second-half of this century. By 2100, BECCS will need to remove 2 Gt/y CO_2, and DACS 3.3 Gt/y (IEA 2023).

This means that a new Green Revolution is now needed, not in agriculture but in the way we collectively do business. The existential threat of climate change must be foremost in our decision-making, and new technologies must be developed to make CO_2 capture an integral part of doing business, and products based on captured CO_2 part of our everyday consumer goods. It is only by spreading the load of CO_2 reduction across every aspect of society that the necessary scale of BECCS and DACS infrastructure can be deployed in time. Policies to reduce greenhouse gas

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[1] http://theconversation.com/carbon-emissions-will-reach-37-billion-tonnes-in-2018-a-record-high-108041

[2] https://www.smh.com.au/environment/weather/australia-weather-2023-hottest-on-record-20231108-p5eij6.html

[3] https://www.climatechange.vic.gov.au/building-victorias-climate-resilience/our-commitment-to-adapt-to-climate-change/adapting-creates-economic-opportunities-and-stronger-communities

emissions to net zero must be strengthened to instead target net negative (see Appendix 1: Manifesto for a New Green Revolution).

Victoria is very well placed to take a leading role in addressing the global warming challenge. The current Labor Government has been proactive in introducing renewable power into the electricity grid, shutting down aging coal-fired power stations, and starting to wind back the state's historical dependence on natural gas. It is also developing what could prove to be one of the State's most valuable resources – the CarbonNet CO_2 transport and sequestration infrastructure. In the Gippsland Basin, Victoria has some of the best geological structures for CO_2 storage in the whole of Australia. In time, the depleted oil and gas fields in Bass Strait will provide 30 - 300 Gt of storage capacity. Now is the time that the State Government should be looking forward to how Victoria can capitalise on this huge natural resource, by using it in combination with lignite to produce low-emissions hydrogen, ammonia and urea, and thereby create new export industries and high-paying jobs.

The process of capturing and storing CO_2 from industrial sources is known as 'carbon capture and storage' (CCS). When the CO_2 is captured from the atmosphere and stored, it is DACS. Once captured, the CO_2 is no longer a waste product, but a potentially valuable resource. If a portion of captured industrial CO_2 is put to good use in some way, it is known as 'carbon capture, utilisation and storage' (CCUS).

In other contexts, taking a waste product and putting it to good use is known as 'recycling'. Extracting as much value as possible from all natural resources, rather than sending them straight to waste, is essential in a more environmentally-sustainable 'circular economy'. To reinforce this connection with an environmentally-sustainable way of doing things, in this report the beneficial use of captured CO_2 is referred to as 'CO_2 recycling'.

While the idea of CO_2 recycling is inherently appealing, in practice it is quite challenging and often quite complex. CO_2 is the end product of combustion and respiration processes, making it a highly oxidised and thermodynamically stable molecule. Upgrading it to more valuable products requires some ingenuity. However, a wide variety of approaches have been developed to add value to captured CO_2, as illustrated in Figure 1 below.

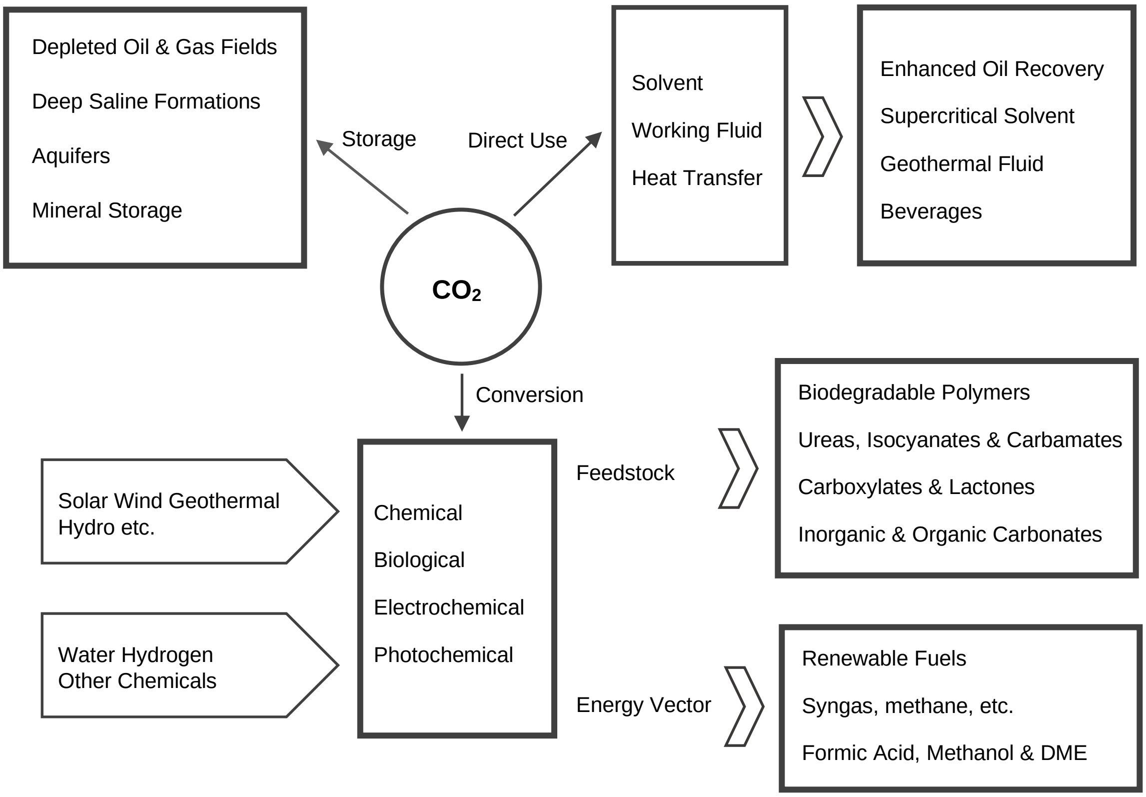

Figure 1: *Pathways to utilisation of carbon dioxide (redrawn from Jarvis & Samsatli 2018)*

The various product opportunities for CO_2 range in market value, depending on the costs associated with their manufacture, as shown in Figure 2 below.

A key component illustrated by the pyramid is that a product’s market value and market size are inversely correlated, i.e., as value goes up, market size decreases. For example, lower profit margins are more closely associated with commodities than with fine or specialty chemicals. It can be difficult to commercialize new technologies for producing commodities due to the low profit margins. One strategy for commercialization is to focus on higher-value specialty and fine products early in the development process, and then pivot toward larger-volume commodity markets as the technology matures. Different CO_2 recycling technology developers are considering approaches at all levels of the pyramid (Council on Environmental Quality 2021).

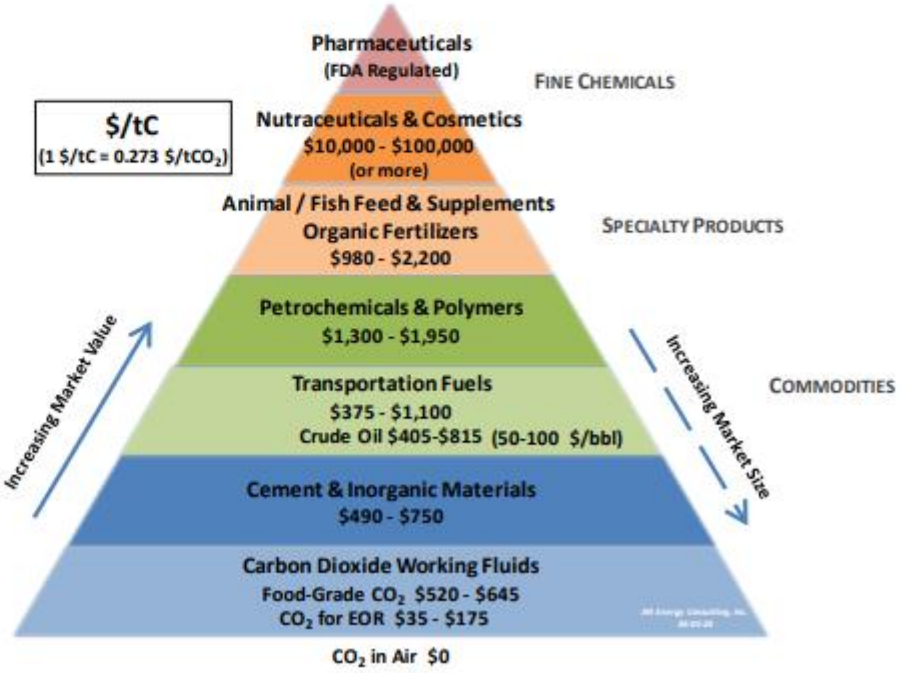

Figure 2: *Market value of various carbon-based goods and services (Council on Environmental Quality 2021)*[4]

In some cases, CO_2 can be used directly without any need for upgrading, e.g., as a solvent, working fluid or heat transfer medium. Such 'direct use' is currently the main way that CO_2 is used by industry.

The only chemical reaction involving CO_2 that proceeds spontaneously, with little input of additional energy, is the reaction with strong bases (containing hydroxide ions, OH^-) yielding inorganic carbonates. This type of reaction has been the subject of intense commercial interest, as a way to produce valuable products and also as a means to capture CO_2 directly from the atmosphere.

It should be noted at this point that there is a direct relationship between CO_2 recycling technologies and DAC. In some cases, the same chemical reactions are involved. In other cases, CO_2 recycling provides a means to add value to captured CO_2, thereby making DAC more financially attractive. Despite this overlap, the topic of DAC (which is interesting and urgently needed), is beyond the scope of this report.

In the majority of cases, converting CO_2 to useful products requires it to be made less oxidised, which is done through the addition of hydrogen (H_2), a reducing agent. This comes at both a cost and an energy penalty. Figure 3 below illustrates how the energy level of CO_2-derived molecules increases with progressive reduction by H_2.

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[4] Note that values are in $/t of carbon, rather than $/t CO_2 (each $/t of carbon equates to 0.273 $/t of CO_2).

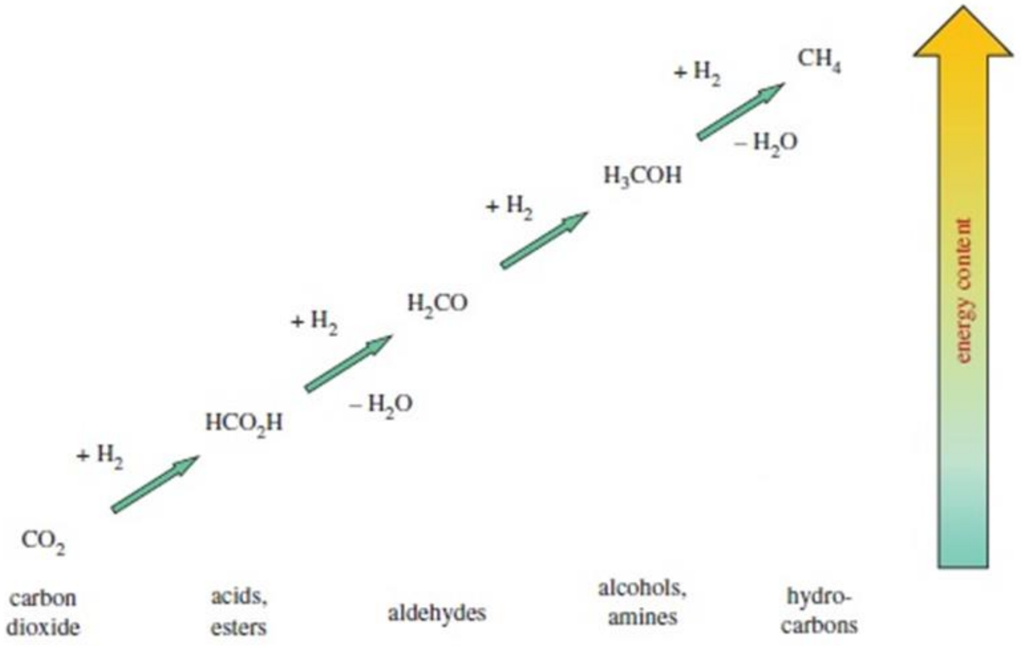

Figure 3: *Adding energy to CO_2 by reduction with hydrogen (Klankermayer & Leitner 2016)*

Such reactions do not proceed spontaneously, but require the provision of energy-rich hydrogen, plus additional energy supplied in the form of electricity, light or heat. A catalyst is also needed, to increase the rate of the reaction. The commercial feasibility of such processes is usually dependent on devising novel process configurations and efficient catalysts to minimise the energy input and production cost (Klankermayer & Leitner 2016).

In some cases, it is possible to employ biological systems, such as plants, algae and microbes, which have evolved sophisticated natural catalytic systems that operate under mild conditions. This generally involves the light-driven photosynthesis reaction, which reduces CO_2 for conversion to sugars, starch and cellulose. In this report, only biological light-driven systems are considered – artificial light-dependent processes are not scaleable (at present), and so are excluded from consideration.

2.2 STRUCTURE OF REPORT

The bulk of this report will consist of an overview of each of the known ways that CO_2 can be utilised commercially, either directly or indirectly. To help provide some structure to the diversity of information that will be presented, the presentation follows the general trend represented in Figure 3 above, following a progression from least to most energy-intensive process. Electrochemical processes, which do not sit easily within this progression, are placed at the end.

Section 3 provides a perspective on the international state of play in CO_2 recycling, based on reviews published over the last five years. From this, a global perspective emerges on what are seen as the best options for scale up (low value – high volume to high value – low volume), that will be both commercially successful and make a meaningful contribution to lowering the State's greenhouse gas emissions. This section also includes perspectives on the barriers to entry experienced by these products, and highlight the need to match policies and resources strategically, aligning codes and standards to avoid delays and wasted money. From this, it is understood that successful commercialisation of cleaner, greener technologies as quickly as possible relies on proactive support at all levels: government, business, and the public.

Section 4 brings forward ACI's conclusions about the most prospective technologies that could be turned into local businesses, generating jobs, etc., while saving the planet. Twelve technologies are put forward as likely contenders, and are given a ranking in terms of technology readiness level and approximate time-frame for development. Each technology is described briefly, and reference is made in relevant sections of the main body of the report. These findings are then cross-referenced against those of the previous reviews, in Section 3. ACI's findings are generally consistent with those of previous reviewers, but ACI has included some promising candidates on the basis of its understanding of the technologies and their potential to be profitably nurtured in Victoria.

The remainder comprises the bulk of the report, providing thematic descriptions of the various types of CO_2 recycling technology, based on different classes of product. A common structure is used for reporting on each of the different options.

Firstly, a brief description is given of each process, the basic chemistry involved, the companies who are championing commercial development of their processes, and updates on notable recent developments. This information is culled from the public domain, scientific literature, and the patent literature. ACI makes no claim to being experts in patent law, so please read the disclaimer at the beginning of the report. ACI makes best efforts to provide accurate information, but this is a fast-moving field (that Australia needs to catch up with) and there are many commercial secrets being kept.

Secondly, a summary is provided of any relevant research work currently under way in Victoria. This information is based on feedback to a survey prepared by ACI using its network of research linkages. It is acknowledged that this information is incomplete; ACI does not (yet) have the necessary contacts in the Victorian chemicals and plastics industries, and organic chemistry researchers within academia, to ensure complete coverage of all CO_2 recycle topics.

Thirdly, ACI provides some commentary on the state of development of the process involved, its readiness for commercialisation, and the opportunities that it presents for new industrial developments in the Latrobe Valley.

The state of development of each process is quantified in terms of a Technical Readiness Level (TRL), ranging from TRL 1 (just a bright idea), through TRL 6 (demonstrated at pilot scale), to TRL 9 (fully commercialised). The definition of each TRL value is provided in Appendix 2. TRL values are assigned by ACI on the basis of the information available and are acknowledged to be subjective.

It would be a challenge to read this report cover-to-cover and absorb all the information presented. The ‘need-to-know’ information is provided in the front sections, leaving the main body of the report as a reference on an ‘if-interested’ basis.

Section 5 of the report includes CO_2 recycle options that involve the direct use of CO_2 for its inherent characteristics as a molecule, whether it be in gaseous, solid or supercritical form. This is the lowest energy input class of applications.

Section 6 includes options for the recycle of CO_2 through biological conversion, using horticulture, microalgae culture and microbial culture. Biological processes are chemically sophisticated, requiring complex sequences of catalytic reactions. However, they have evolved to operate under mild conditions, which we can use to our advantage.

Section 7 covers inorganic carbonation, which is another low energy level class of chemistry. The chemical reactions occur spontaneously, needing only a small input of energy to boost them along. This aspect of CO_2 recycling includes processes for producing ‘green’ construction materials and simple carbonate salts, and offers great potential for large-scale deployment and significant CO_2 reductions.

Section 8 includes chemical processes for CO_2 recycle that require a higher energy input, and the use of catalysts to help overcome the energy barrier of breaking C=O bonds. This includes the production of valuable organic carbonates (linear, cyclic, polycarbonate polyols and polymers) and a wide variety of reaction intermediates and fine chemicals.

Section 8 also includes chemical processes that involve catalytic reduction of CO_2 with hydrogen. This requires even higher energy, but can be used to synthesise valuable commodities such as formic acid, methanol, carbon monoxide, synthesis gas, methane (synthetic natural gas) and hydrocarbon olefins and fuels.

Section 9 includes processes for recycle of CO_2 using a combination of electrical energy and catalysis to electrochemically convert CO_2 into syngas, formic acid and carbon nanofibres.

Of all the technologies covered by this report, those in Sections 8 and 9 are those that are most intimately linked to renewable energy and the availability of abundant, low-cost low-emission hydrogen. In most, but not all, cases they cannot compete economically with the current fossil-based processes, but their basis in clean energy sources makes them an environmental necessity. The race is on to find the winners and crack the big markets.

This report has not been written with a view to eventual publication. It is far too long to publish in a journal, and is essentially based on a series of previously published topic reviews, strung together and updated. The images included do not come with permission from the copyright holders for publication so, while the information in the text provided is not confidential, it is not permissible for the images to be placed in the public domain in any form. Thank you for your cooperation in avoiding litigation.

3 A Global Perspective on CO_2 Recycling

3.1 PREVIOUS REVIEWS OF CO_2 RECYCLING

International interest in the topic of CO_2 recycling has led to publication of a number of reviews seeking to identify the most prospective technologies for commercialisation. As noted above in relation to Figure 2, technology developers may choose to target either high-volume low-value products or low-volume high-value products, so there is no universal consensus on which is the best approach. In this section, the findings from a number of recent reviews are described, to help provide a context for consideration of CO_2 recycling options in Victoria.

In 2017, researchers at Imperial College London looked into the opportunities for CO_2 recycling in the UK. The considerations involved in evaluating the various options are summarised in Table 1 below.

Table 1: *Factors influencing CO_2 recycling options in the UK (Alberici et al. 2017)*

Technology	**TRL level**	**UK demand in 2030 (ktCO2/yr)**	**Location factors and identified regions**	**Key barriers**
Carbonation (via “Accelerated Carbonation Technology“)	8	5-43	o Key factors: availability of waste stream, CO_2 source, market access o Fly ash: co-location with concrete block manufacturers o Steel plants, cement plants, or other historical deposits plants: located at, or near to, the site	o Availability of waste materials o Planning legislation o Long-term track record demanded by construction sector
Concrete curing	7-8	0-100	o Pre-cast concrete: installed at existing concrete plants o Ready-mix concrete: no specific location factors as building sites spread over the country	o Long-term track record demanded by construction sector
Novel cements	3-6	0	o Located near to a port since we are unaware of any significant magnesite deposits in the UK	o Long-term track record demanded by construction sector
Horticulture	9	108-218	o Reliable source of all-year around CO_2 (and heat) o Possible co-location with waste-to-energy or biomethane plants o Identified suitable areas: East Yorkshire/Hull area, Lea Valley and Thanet	o Limited types of industrial facilities that meet supply and quality requirements o Growers that have recently installed CHP systems are likely to have no (or limited) demand for industrial CO_2
Polymer processing	8	0-100	o Proximity to chemical industry clusters and downstream production processes using the CO_2-based polyols to provide opportunities for industrial symbiosis o Identified suitable areas: Teesside, Grangemouth, Fawley and Hythe	o Lack of plants (even at large pilot scale) producing the polymers in the UK o Risk averseness around new products
Synthetic methane	7-8	0-18	o Access to low cost electricity (for H_2 production), potable water and gas	o High costs associated with the synthetic methane process

			connection that can accept the flow produced o Possible synergies with biomethane injection plants, bio-SNG plants, water treatment plants, fermentation processes	
Synthetic methanol	8	0-145	o Access to low cost electricity (for H_2 production), potable water o By-product H2 from chlor-alkali production facilities (Runcorn) or coking gas from steel manufacturing (Port Talbot and Rotherham)	o High costs associated with the synthetic methanol process o Restriction on blending levels o Lack of existing methanol fuelling infrastructure

This review found that each technology is at a different stage of development and faces different barriers to reach full commercialisation. However, some of the things that they have in common are that the use of CO_2 as an input material can significantly lower the carbon footprint compared to using fossil fuel-based feedstocks. In some cases, products incorporating CO_2 are reportedly cheaper to produce than their conventional counterpart (e.g., carbonated aggregate for construction, CO_2-based polymers), but the market is hesitant to widely adopt the products. In other cases, the cost is still too high (e.g., methanol, synthetic methane) and some technologies have fundamental limitations which will limit application even if very significant improvements can be made. Of all the technologies assessed, mineral carbonation was found to offer the greatest carbon abatement potential (Alberici et al. 2017).

It was recommended that Government and other stakeholders could facilitate commercial development of CO_2 utilisation technologies in the UK by:

- Raising awareness of CO_2-based products among both private sector parties and the wider public. For example, through detailed life cycle analyses, support for material testing trials, development of product standards and labelling schemes, and promoting the benefits and business opportunities of CO_2 recycling.
- Providing financial incentives to accelerate investment in CO_2 recycling technology development. For example, through Government and industry co-funding for a CO_2 recycle demonstration competition to help companies bring technologies to market; by providing (financial and technical) support for R&D in CO_2 recycle technologies, particularly with a view to de-risking and scaling up promising existing innovations rather than promoting new innovations; and by providing government guarantees, or providing access to low-cost finance, to help de-risk first-of-a-kind CO_2 recycling projects.
- Strengthening knowledge transfer involving key stakeholders including CO_2 emitters and potential users of CO_2-based products. For example, through stimulating multi-stakeholder discussion of CO_2 recycling within existing networks (e.g., the scientific community, industry (including cluster and sector associations), investors, Local Enterprise Partnerships (LEPs) and national government) to identify potential quick wins and opportunities for industrial symbiosis (Alberici et al. 2017).

In 2018, Pan and co-workers published the graphic shown in Figure 4 below, which categorised CO_2 recycling technologies in terms of their relative technological "readiness" and the likely time needed for commercialisation.

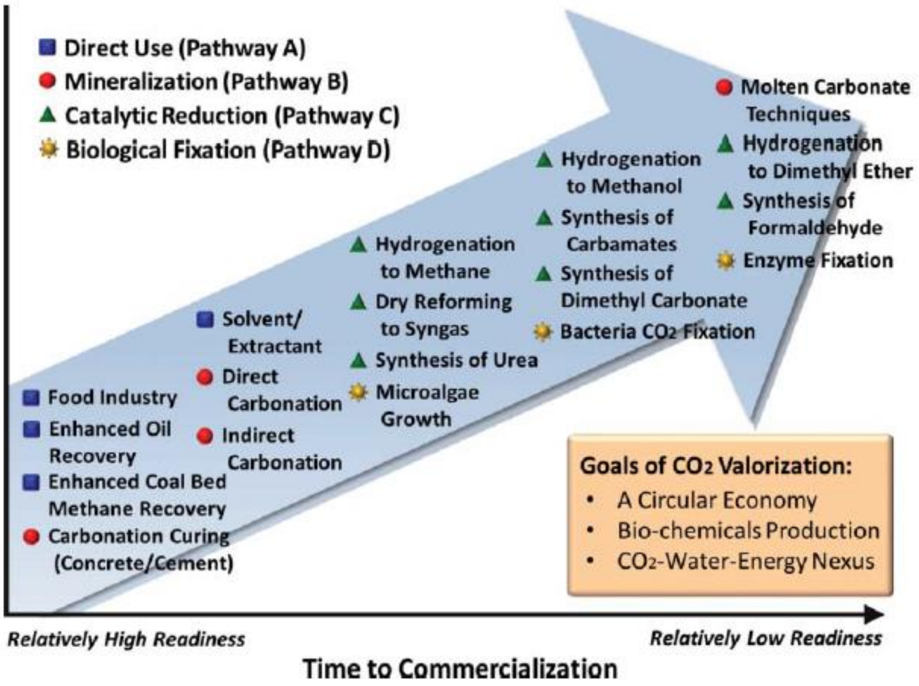

Figure 4: *Roadmap of valorization technologies for captured CO_2 (Pan et al. 2018)*

This analysis identified direct use of CO_2 and indirect carbonation technologies as having the shortest time to commercialisation.

In 2019, the International Energy Agency (IEA) published a review on the opportunities for CO_2 recycling. It reported that this topic is generating significant global interest, reflected in increasing support from governments, industry and investors. Global private funding for CO_2 recycling start-ups reached nearly US$1 billion over the previous decade. Interest and investment in this area is expected to increase as, in the transition to a net-zero economy, CO_2 will increasingly have to be sourced from biomass or the air. Conversion of CO_2 to value-added products will aid this transition, but the market for CO_2-based products will likely remain relatively small in the short term. Early opportunities, such as the use of CO_2 in building materials, can be stimulated through Government support for product testing trials and updating of standards, and through public procurement of low-carbon products with verifiable climate benefits (IEA 2019).

The IEA concluded that CO_2 recycle can deliver climate benefits where the application is scalable, uses low-carbon energy and displaces a product with higher life-cycle emissions. Quantification of these benefits is needed to inform future policy and investment decisions. Figure 5 below shows the outcome of a high-level screening by the IEA of the theoretical potential for CO_2 recycle and the likely climate benefits. This analysis found that fuels have the largest potential due to their vast market size, while building materials show the greatest climate change mitigation potential mainly because of the low energy requirements and the permanent retention of carbon in the product (IEA 2019).

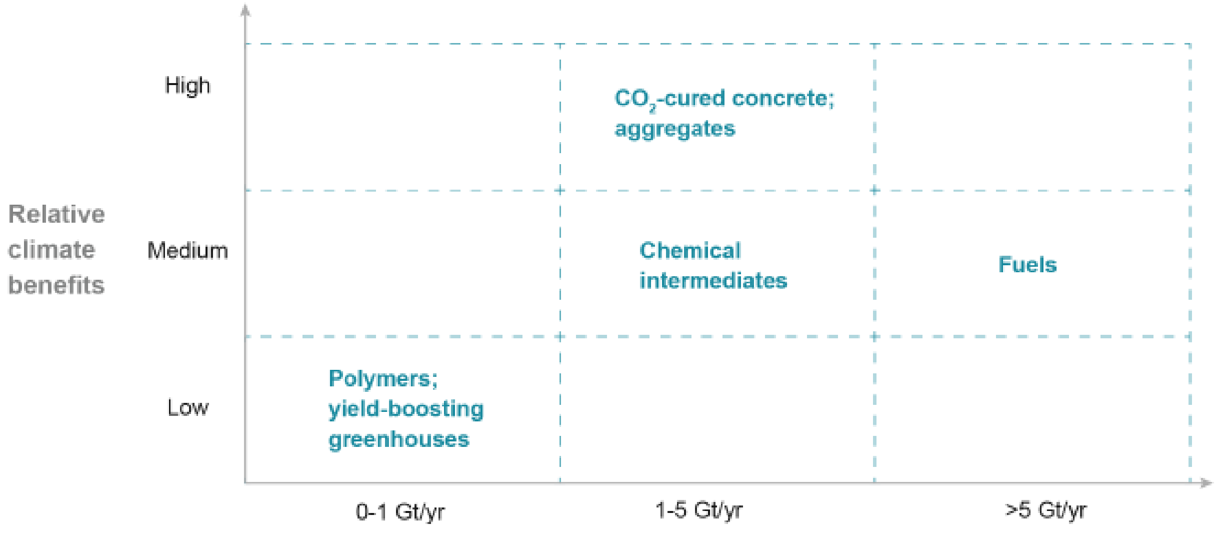

Figure 5: *Theoretical potential and climate benefits of CO_2-derived products and services (IEA 2019)*

The IEA expects that the market for CO_2-derived products and services will remain small in the short term. Individual markets are either small in nature (polymers, greenhouses), limited to locations with favourable conditions (methane, methanol) or face other barriers for fast deployment, such as building standards and codes (building materials) (IEA 2019).

Also in 2019, Chauvy and co-workers undertook a rigorous analysis of CO_2 recycling alternatives using a multi-criteria assessment that included technical, economic, energetic, environmental and market considerations. The options that appeared to be viable, with a high level of maturity, and suitable for near-term implementation, involve production of (i) compounds that have a low unit price but significant market volume, including methanol, methane, calcium carbonates, microalgae, sodium carbonates, urea, syngas and ethanol; and (ii) compounds that have a high unit price but low market volume, such as dimethyl carbonates, polycarbonates, formic acid and salicylic acid (Chauvy et al. 2019).

Table 2: *CO_2 recycling options with near-term potential (Chauvy et al. 2019)*

CO_2-based compound	CO_2-conversion process
Calcium carbonate	Mineral carbonation
Dimethyl carbonate	Organic synthesis
Ethanol	Microbial process
Formic acid	Electrochemical reduction

Methane	Hydrogenation
Methanol	Hydrogenation
Microalgae	Biological process
Polycarbonates	Organic synthesis
Salicylic acid	Organic synthesis
Sodium carbonates	Mineral carbonation
Syngas	Dry reforming
Urea	Organic synthesis

These researchers also assessed the Technology Readiness Level (see Appendix 2) and likely timeframe for commercial deployment of each technology, as shown in Figure 6 below.

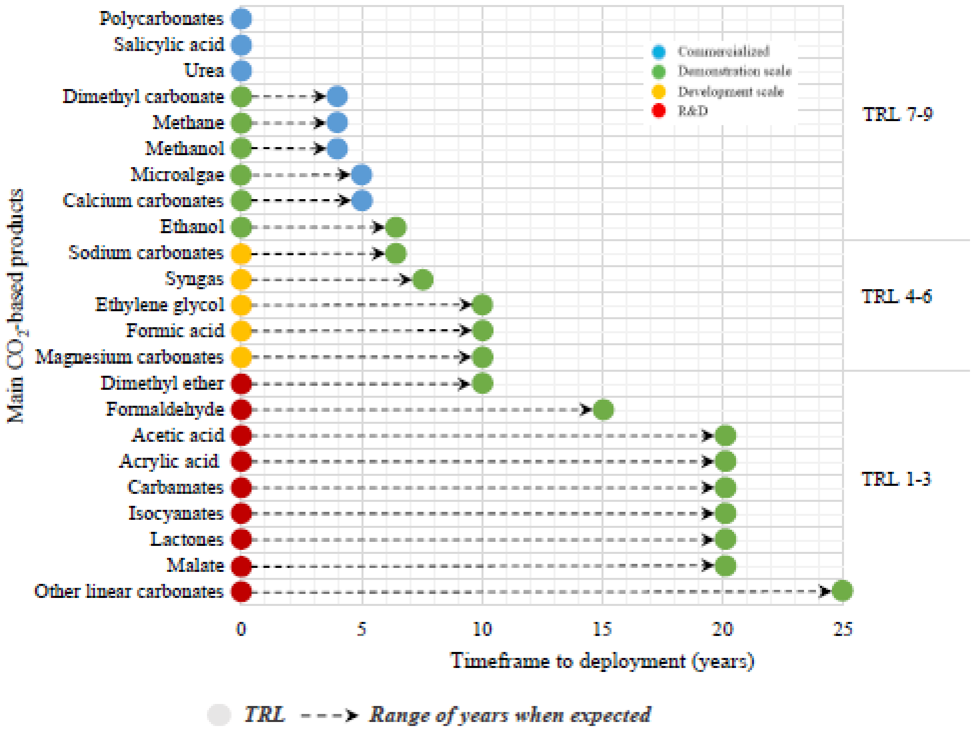

***Figure 6:** TRL and timeframe for deployment of CO_2-based products (Chauvy et al. 2019)*

In 2021, CSIRO published a *CO_2 Utilisation Roadmap* from the Australian perspective (Srinivasan et al. 2021). Given that cost-effective CO_2 recycling applications are still emerging, the purpose of the CSIRO roadmap was to inform the debate about the associated risks and opportunities in the Australian context. The report focussed on four areas: direct use of CO_2, mineral carbonation, conversion of CO_2 to chemicals and fuels, and the biological conversion of CO_2.

CSIRO found that Australia is well placed to play a leading role in deployment of CO_2 recycling technologies, with access to abundant renewable energy to power processes and large quantities of hydrogen as feedstock, plus substantial quantities of other inputs, such as mine tailings or minerals for carbonation. However, it found that understanding of CO_2 recycling is still nascent in Australia and globally, and requires clear communication at government, industry and public levels.

The roadmap developed by CSIRO included aspects of both CO_2 supply and CO_2 use, as shown in Figure 7 below. In the transition to net-zero, major industrial emitters of CO_2 will increasingly have to deploy CO_2 capture and direct air capture (DAC) of CO_2 will have to be rapidly scaled up and deployed across multiple sites. Applications for captured CO_2 will progress from direct use in the immediate-term to progressive demonstrations and commercialisation of mineral carbonation, chemicals and fuels, followed in the longer-term by biological processes (Srinivasan et al. 2021).

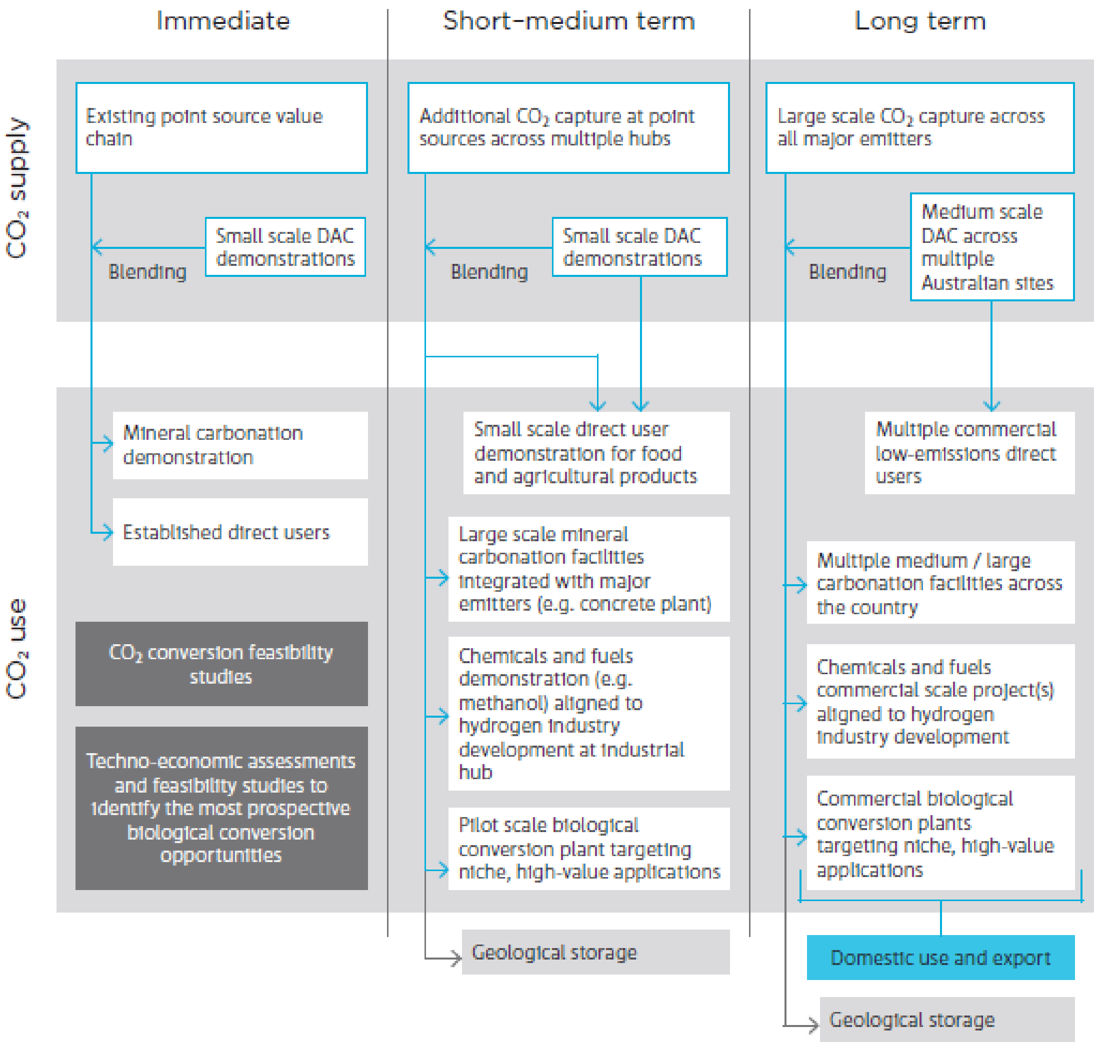

Figure 7: *Roadmap to scale-up of CO_2 recycling (Srinivasan et al. 2021)*

CSIRO also provided recommendations to facilitate the rapid deployment and upscaling of the most prospective CO_2 recycling technologies, which include (Srinivasan et al. 2021):

1. Diversify and engage across the value chain and multiple CO_2 recycling applications:
    - Engagement and close collaboration to avoid duplication, minimise risk and attract investment.
    - Clear communication of CO_2 recycling and its role in the decarbonisation challenge will be vital.
    - Engagement and integration with existing strategies and green mechanisms, such as the development of the circular economy, will promote CO_2 recycling uptake.
2. Use CCU as part of a portfolio of decarbonisation solutions.
3. Explore incentives and minimise barriers to entry:
    - Green premiums can be reduced by driving down the cost of CO_2 recycling, by rising costs for the carbon intensive incumbent, or a combination of both.
    - CO_2 abatement costs should be considered alongside technology improvements, revenue potential, secondary benefits and lifecycle assessments.
    - Mechanisms and incentives can help to bridge the final gap, including:
        - Tax credits and subsidies
        - Carbon intensity accreditation and guarantees to reward low carbon investments
        - Quotas to guarantee offtake of CO_2-based products
        - Commercial mechanisms to demonstrate and scale technologies.
4. Use CCU to support or de-risk investment in existing and planned infrastructure
    - The most efficient deployment of CO_2 recycling technologies will be at sites where it can leverage infrastructure that already exists or is planned for construction. As such, deployers should consider how CO_2 recycling can add value to industrial and energy hubs, and de-risk investment.
    - For example, Figure 8 below illustrates a concept for a methanol hub, which makes use of hydrogen and CO_2 capture infrastructure to produce methanol and subsequently upgrade methanol to other value-added products.

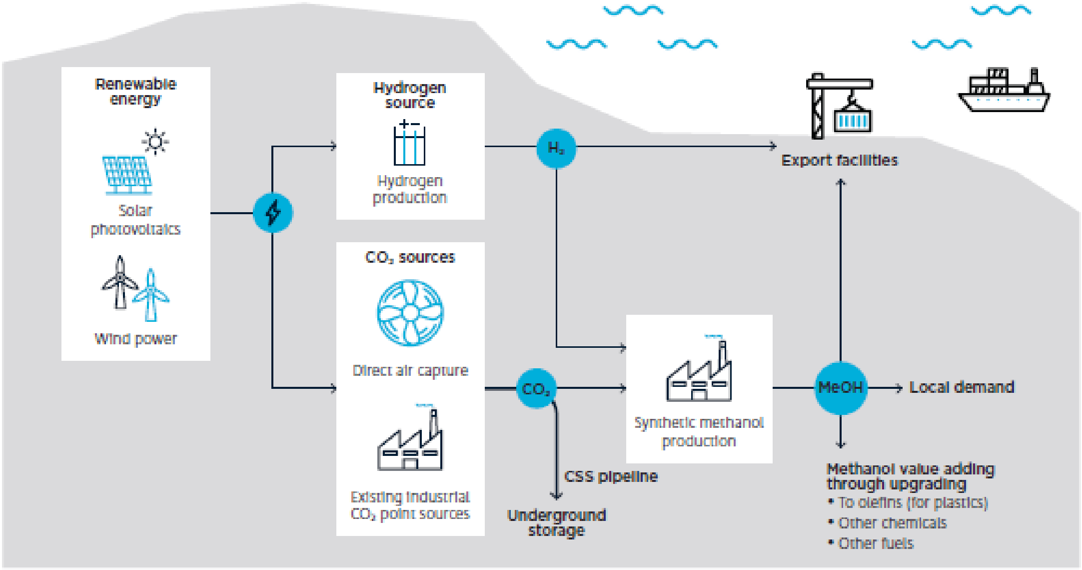

Figure 8: *Methanol hub involving existing/planned infrastructure to complement and de-risk investment (Srinivasan et al. 2021)*

Also in 2021, the IEAGHG published a technical report which provided a comparison of the various CO_2 recycling pathways. The options investigated are shown in Table 3 below. In this table, 'Market Size' indicates the 2019/2020 production of conventional product in units of tonnes of product, to provide an indication of size of the market available for substitution.

Table 3: *Summary of CO_2 recycling options evaluated (IEAGHG 2021)*

Category	Commodity	Market Size	Utilisation Method(s)
Building Materials	Concrete	30 Gt	Forming mineral carbonates
	Aggregates - Manufactured	1 Gt	Forming mineral carbonates
Chemicals	Methanol - Chemical Intermediate	80 Mt	Hydrogenation
	Formic Acid	1 Mt	Hydrogenation / Electrochemical reduction
	Dimethyl Carbonate (DMC)	90 kt	Reacting CO_2 and epoxides / Reacting CO_2 and methanol
Polymers	Polycarbonate	4 Mt	Reacting CO_2 and epoxides
	Polyols for Polyurethane	12 Mt	Reacting CO_2 and epoxides (catalytic co-polymerisation)
Fuels	Middle Distillate Hydrocarbons	3 Gt	Hydrogenation
	Synthetic Methane	2 Gt	Hydrogenation
	Dimethyl Ether (DME)	500 Mt	Hydrogenation
	Ethanol	100 Mt	Electrochemical reduction
	Methanol - Gasoline Blending	30 – 170 Mt	Hydrogenation

IEAGHG commissioned Element Energy, UK, to undertake this study, with the aim of identifying areas of strength and weakness within individual routes, comparing different CO_2 recycling pathways, and identifying common drivers, barriers, and enablers. To do this, each commodity was assessed under four primary criteria: CO_2 mitigation potential, market uptake potential, technical scalability, and other impacts. To provide granularity, each primary criteria was assessed according to an additional set of sub-criteria. The outcomes of this study are summarised in Figure 9 below.

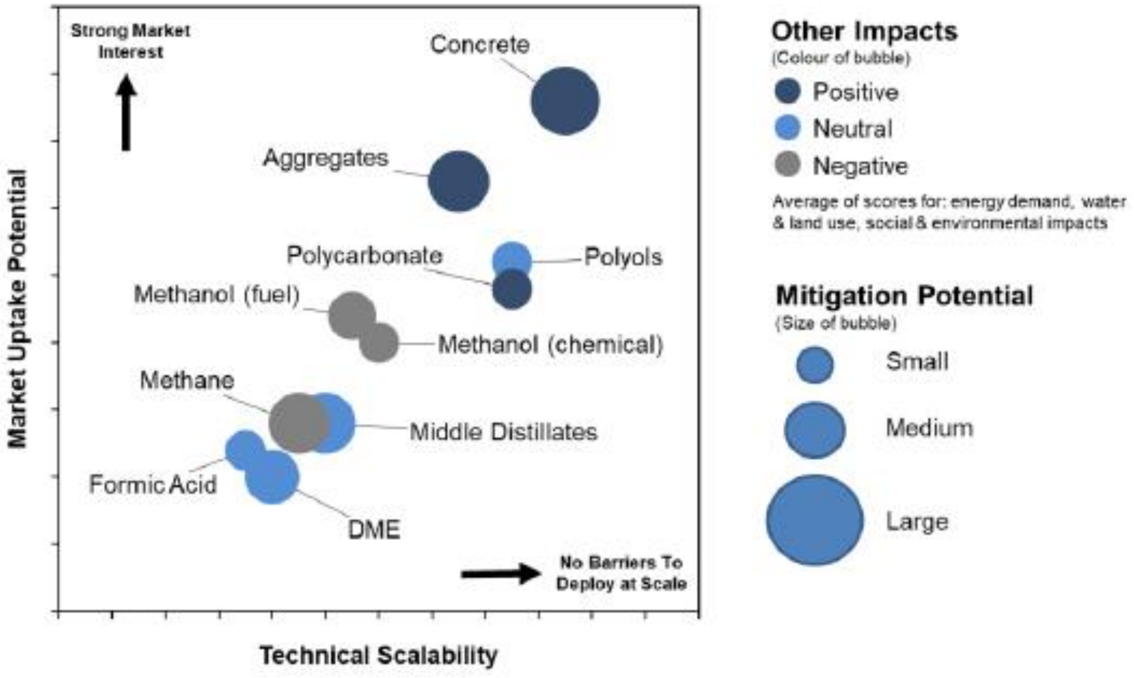

Figure 9: *Summary of the comparative assessment outcome (IEAGHG 2021)*

In this diagram, the colour of the circles is mainly a reflection of the permanence of CO_2 sequestration in the products, with building materials and non-recyclable polycarbonate plastics being essentially permanent, fuels being non-permanent, and chemicals occupying an intermediate position.

This study found that the potential scale of life cycle emissions abatement was greatest for fuels and building materials, which have large existing markets, than for chemicals and polymers, for which existing markets are orders of magnitude smaller. Many CO_2 recycling routes have been demonstrated at an industrially relevant scale, and CO_2-cured concrete, waste-to-aggregates, methanol, and polycarbonates technologies are ready for commercial deployment. The building materials and polymers categories were found to have greatest potential under existing market drivers, and in some cases have already been adopted in commercial settings.

It was found that the chemicals and fuels categories are considerably more expensive than conventional fossil-based production routes. This was largely because of high energy requirements to produce the hydrogen feedstock, but also from the low yields and high catalyst costs of some of the lesser developed routes. Nevertheless, there is considerable political and regulatory support for sustainable products within the fuels sector, with some regions introducing mandates or standards that could lead to increased uptake of CO_2-based fuels (IEAGHG 2021).

Apart from technical or energy cost barriers, the IEAGHG recognised that development of CO_2 recycling technologies can also be impacted by regulatory or policy factors and market perceptions. To address these issues, the following recommendations were made:

- Researchers, institutions, and manufacturers can work to improve awareness of life cycle emissions for existing products, engage with the public and with policy makers, and improve understanding of the benefits and limitations of CO_2 recycling routes.
- Governments can encourage innovations and developments in CO_2 recycling by providing funding for research programmes and demonstration projects, or through other support mechanisms.
- Policy makers can work to enable CO_2 recycling by introducing support mechanisms that allow it to receive recognition for sustainability benefits and compete on a more level-playing field with conventional products.
- Policy makers and regulators should ensure that CO_2-based products are incorporated appropriately into existing support schemes, regulations, and product standards. For example, by moving to performance-based standards rather than prescriptive requirements (IEAGHG 2021).

The last point was reiterated by Li et al. (2022), in a review of CO_2 recycling for the construction industry. They made the point that building standards tend to be prescriptive rather than performance-based, specifying the composition of the materials that can be used instead of the performance requirements. Even though carbonation cured building products have been found to have comparable or even superior performance when compared to ordinary Portland cement-based concrete, they do not necessarily meet the composition specified under the relevant standard. The lack of relevant building standards and codes makes it difficult to commercialise these products on a large scale.

These reviewers recommended that increased uptake of CO_2-based products within the construction industry requires a series of coordinated schemes leading to large-scale demonstration, further supported by incentives for the public and private sectors to invest in and consume these products (Li et al. 2022).

In broad terms, a consensus emerges from these previous reviews which is consistent with the conclusions of the present study. This point is addressed in Section 4.1.4 below

3.2 FUNDING SUPPORT FOR DEVELOPMENT OF CO_2 RECYCLING

To date, the European Union has been by far the major funder of CO_2 recycling projects. From 2014-2020, Horizon 2020 was the EU's research and innovation funding program, with a budget of nearly €80 billion. The Work Program 2015-2016, ‘Secure, Clean and Efficient Energy’, provided funding of €6-8 million for scale-up of processes to produce high-volume added value products from CO_2 and demonstrate the technical and economic feasibility in an industrially relevant environment. Funding was open for technologies at TRL 5-6, with a target of TRL 6-7 by the end of the project.[5] This funding stimulated collaborative projects involving dozens of research institutions and major European companies, including Linde, ThyssenKrupp, BASF, Repsol, Bayer, Siemens, Solvay, Total, GRTgaz and Audi. Japanese companies such as Mitsui Chemicals and Mitsubishi Hitachi Power Systems were also involved (Marzano et al. 2015).

One of the Horizon 2020 projects was LEILAC (Low Emissions Intensity Lime And Cement), which received €12 million funding. Interestingly, LEILAC involved a pilot scale demonstration in Belgium of a novel direct calcination process developed by Calix in Bacchus Marsh, Victoria. In direct calcination, an inner tube containing steam and limestone is heated by the combustion of fuel in the outer tube[6] (see Figure 10 below). The steam can be easily separated from the CO_2 from calcination by condensing it out, producing a CO_2 stream with 95% purity. The Leilac-1 pilot plant has been operating successfully since 2019, and a FEED study has been completed for Leilac-2, a 100,000 t/y demonstration plant to be built at Heidelberg Materials' cement plant in Hannover, Germany.[7]

Figure 10: *The direct calcination technology, and an impression of the Leilac-2 demonstration plant*

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[5] http://ec.europa.eu/research/participants/data/ref/h2020/wp/2016_2017/main/h2020-wp1617-energy_en.pdf

[6] https://www.imperial.ac.uk/a-z-research/clean-fossil-and-bioenergy/research/current-research-projects/leilac-cheap-efficient-carbon-capture-for-the-cement--lime-industries/

[7] https://www.leilac.com/project-leilac-2/

Horizon 2020 was succeeded by Horizon Europe, which is the EU's key funding program for research and innovation with a budget of €95.5 billion until 2027.[8] Part of this funding contributes to P4Planet, a public-private joint program in collaboration with A.SPIRE,[9] a private European Association representing more than 180 industrial and research process stakeholders from more than 20 countries spread throughout Europe.[10] Some of the projects currently funded through this collaboration involve conversion of waste CO2 into methanol and other chemicals, carbon-negative minerals for construction products, sustainable PET textiles, polyester polyol intermediates for polyurethane plastics, and white oils and high molecular weight aliphatic waxes.[11]

In recent years, the USA has begun to actively promote CO_2 recycling technology development. In 2015, the NRG COSIA Carbon XPRIZE was launched as a five-year global competition to develop breakthrough technologies to convert CO_2 into high value products. The joint winners of the NRG COSIA Carbon XPRIZE were CarbonCure Technologies (Section 7.1.3.1.4) and CarbonBuilt (Section 7.1.3.1.3).[12]

In 2021, the US enacted the Infrastructure Investment and Jobs Act (IIJA), which included over $12 billion to be spent on CCS over five years. The legislation includes funding for CCUS RD&D, CO_2 transport and storage infrastructure, carbon utilisation market development, four regional DAC with carbon storage hubs, and a DAC Technology Competition (Global CCS Institute 2022).

In 2022, the US introduced a significant stimulus for CCUS investment through the Inflation Reduction Act (IRA), providing tax credits of US$85/t for CO_2 captured from industrial facilities and permanently stored, US$180/t for CO_2 captured by direct air capture (DAC) and permanently stored, and US$60/t for CO_2 captured and used, provided emissions reductions can be clearly demonstrated. The IRA was intended to incentivise the industrial sector to decarbonize and promote development of DAC.[13] The IRA paved the way for an array of impactful tax credits, including the Blender's Tax Credit, the Clean Fuel Production Credit, sections 45Q (Carbon Capture and Utilization), 48C (Advanced Energy Projects), and 45V (Clean Hydrogen Production).[14]

In February 2023, the Captured Carbon Utilization Parity Act was introduced, seeking to increase the tax credit for carbon utilization projects to match the incentives for storage projects. Under this Act (not yet approved), tax credits of US$85/t would be available to industrial and power-generation facilities seeking to reuse captured carbon in the manufacturing of low- and zero-carbon products,

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[8] https://research-and-innovation.ec.europa.eu/funding/funding-opportunities/funding-programmes-and-open-calls/horizon-europe_en

[9] https://www.aspire2050.eu/p4planet/about-p4planet

[10] https://www.aspire2050.eu/aspire/the-association

[11] https://www.aspire2050.eu/aspire/the-association

[12] https://www.xprize.org/prizes/carbon/articles/xprize-announces-the-two-winners-of-20m-nrg-cosia-carbon-xprize-with-each-team-creating-valuable-products-out-of-co2-emissions

[13] https://www.catf.us/resource/carbon-capture-inflation-reduction-act/

[14] https://medium.com/@twelve.CO2/the-inflation-reduction-act-one-year-later-f19cb2c0c33

and US$180/t for DAC projects reusing captured carbon to manufacture products of economic value.[15]

Until very recently, there has been little support for CO_2 recycling in Australia. CCS research has been funded through GCCSI, CSIRO, ANLEC R&D, CO2CRC and Brown Coal Innovation Australia (now ACI), but this support has fallen away dramatically. Research on CO_2 recycling is currently fragmentary and uncoordinated, with the known activities in Victoria documented in this report.

The Australian Government has recently established the Carbon Capture Technologies Program (CCTP), which provides grants of up to $15 million to organisations undertaking projects that support CO_2 capture and CO_2 utilisation technologies. Examples of projects that the CCTP may support include:

- the development of a pilot direct air capture facility with new carbon dioxide adsorbent materials to capture CO_2 from the atmosphere.
- the conversion of CO_2 to create building materials, aviation fuels, and chemicals such as urea.
- demonstration of CO_2 capture technology based on adsorption, absorption, membranes, or minerals, for use in hard to abate sectors.[16]

EOI applications for Stage 1 of the CCTP closed on 31 October 2023, and successful applicants for Stage 2 (application) have not been announced at the time of writing.

It is apparent, based on the level of R&D funding, that recognition of the potential value of CO_2 recycling is much lower in Australia than in the European Union or United States. It is telling that a Victorian company, Calix, was successful in gaining EU funding for pilot-scale demonstration (and further scale-up) of its direct calcination technology, but not in Australia.

Given the urgency with which the climate change emergency must be addressed, new thinking is required on how to stimulate and support the development, demonstration and commercialisation of CO_2 capture and recycle technologies in Australia. In the absence of any kind of pricing mechanism that reflects the value to society of CO_2 capture and recycle, market forces alone will not deliver the necessary outcomes.

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[15] https://www.bakerlaw.com/insights/bipartisan-bill-seeks-further-tax-incentives-for-carbon-capture-and-utilization-projects/

[16] https://www.dcceew.gov.au/climate-change/emissions-reduction/carbon-capture-use-storage

4 ACI Synthesis of CO_2 Recycling Options for Victoria

4.1 OPPORTUNITIES FOR CO_2 RECYCLING IN VICTORIA

4.1.1 Summary of Identified Opportunities

The field of CO_2 recycling is very diverse and very dynamic. We are presently witnessing the birth of a whole new class of industries, so it is timely to understand where the opportunities for Victoria may lie. The bulk of this report comprises a comprehensive survey of the range of CO_2 recycling processes that are under development, including the chemistries involved, the companies involved in demonstration and commercialisation, and any relevant local research activities under way. In each case, ACI provides commentary to consider the implications and potential opportunities from a Victorian perspective. This does not make for light reading, so the purpose of this section is to provide a synthesis of the main opportunities identified by ACI that could profitably be developed in Victoria.

The most important point to highlight is that Victoria's Latrobe Valley is, or will be, uniquely endowed with valuable natural resources that are ideal for developing a local industrial ecosystem of businesses based on CO_2 recycling. This is very good news for a region that will need industrial renewal as the power stations progressively shut down. The other good news is that the opportunities are mainly around high-volume low-value products that have the greatest potential for CO_2 sequestration, and thus can contribute significantly to the State meeting its emissions reduction targets.

Figure 11 below gives a high-level overview of the type of industrial ecosystem that could be established in the Latrobe Valley, and the range of new value-added products that could contribute to the local economy.

The scenario depicted looks forward to a point in the not-too-distant future when gasification of lignite and/or biomass is an established commercial process and there is an abundance of inexpensive hydrogen and CO_2 available as feedstocks. The hydrogen is mainly produced for the export market, either in liquefied form or after conversion to ammonia. Stockpiles of fly ash are being remediated, and cultivated industrial hemp provides seeds for refining and renewable biomass for gasification. Not shown, but implied, is the availability of renewable wind and solar energy. Possibly, by that time, the geothermal energy resource in the Latrobe Valley may also become available. Electrolysis is being used to produce green hydrogen, and both direct air capture (DAC) and biogas produce carbon-neutral CO_2 for upgrading.

Thirteen opportunities that have been identified for CO_2 recycling, making use of these resources, are briefly summarised in Table 4 below. A more detailed description is provided in the following subsection, cross-referencing relevant sections in the main body of report.

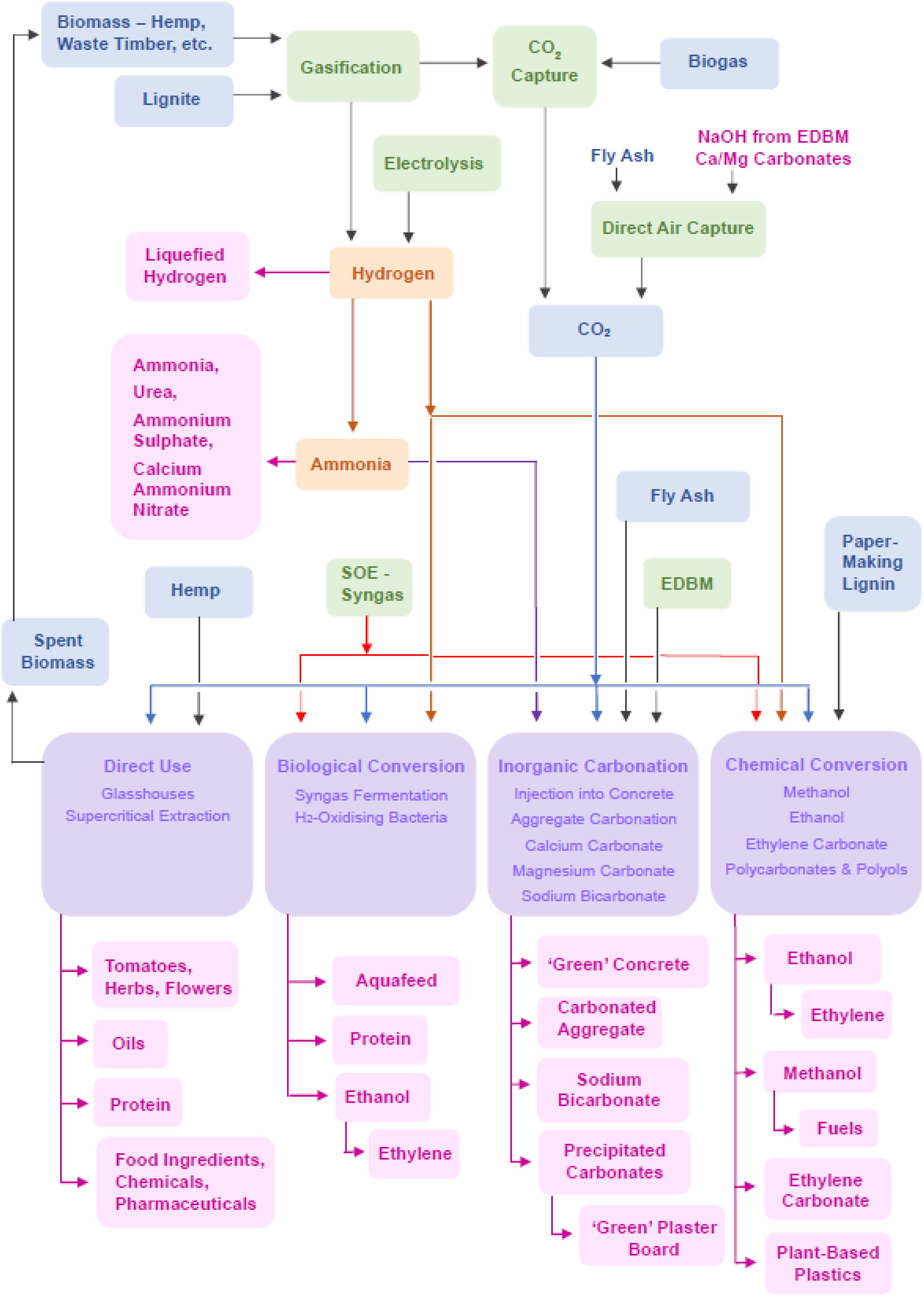

Figure 11: *Identified prospective opportunities for CO$_2$ recycling in Victoria*

Table 4: *Summary identified opportunities for CO_2 recycling in Victoria*

CO_2 Recycling Technology	Product Opportunities Arising	Developmental Status	Rationale for Selection
Urea	Import replacement of a major fertiliser used in Australian agriculture.	Commercial and gasification tested by 2 commercial vendors.	Actively being actively investigated for commercialisation in Victoria.
Carbonation of concrete	Reduced emission intensity of concrete in construction and infrastructure projects.	Commercial and now available in Australia.	CO_2 alone gives an immediate reduction in a major industry sector. Potential to double the reduction using baking soda.
Glasshouse horticulture	Reduced use of CO_2 produced by natural gas combustion in glasshouse production of tomatoes, herbs, flowers, pharmaceutical cannabis, etc.	Already used commercially in some places overseas, but not yet widespread in Australia.	Immediate boost to an existing horticulture industry in the Latrobe Valley. Many product opportunities. Potential for domestic and/or export markets. Opportunities for value-adding using S-CO_2. Biomass waste can be gasified to green hydrogen.
Supercritical CO_2 processing (S-CO_2)	Solvent-free extraction of oils and de-fatting of seed proteins for food ingredients; water-free textile dyeing.	A small food ingredients company in Tasmania, but otherwise not yet commercialised in Australia.	New business opportunity in water-free textile dyeing. Potential for opportunities in defatting of hemp seeds, fruit/vegetable powders, natural colours and flavours, edible and pharmaceutical oils, bioingredient extracts (e.g., hop, pharmaceutical cannabinoids).
Bipolar membrane electrodialysis (EDBM)	Production of acids and alkalis from simple salts using renewable energy, producing alkali for use in CO_2 capture, production of sodium bicarbonate, etc.	Commercially available, used in water industry.	Versatile technology, enabler of new opportunities, compatible with renewable energy. Produces NaOH for production of baking soda, carbonation of fly ash, and DAC.
Carbonated fly ash	Transformation of a hazardous waste into aggregate for 'green' concrete.	Commercialised overseas, but hindered by prescriptive building standards.	Simple chemistry. Ideal way to monetise the massive amount of heritage waste fly ash in the Latrobe Valley. Potential for a variety of low-emissions concretes and

			building materials for the construction industry. Links to Ca/Mg carbonate and DAC.
Ca/Mg carbonate	Additive for ‘green’ concrete and plasterboard.	Commercialised overseas, and being investigated by Mineral Carbonation International in NSW.	Synergistic with baking soda production. Direct link to DAC, and route to adding value to DAC.
Syngas by SOE	High efficiency production of syngas using renewable energy, key enabler for many other products.	Under development by CSIRO and collaborators.	Syngas a versatile industrial chemical feedstock. SOE is more economical at small scale than gasification. Scale appropriate for biological conversion to ethanol or edible biomass.
Methanol	Important chemical industry feedstock.	Commercial overseas, but more expensive than conventional product. Research needed for more efficient catalyst.	A major industrial chemical feedstock. Research interest/expertise in Victoria to build upon.
Ethanol	Important biofuel and precursor to ethylene, a major industrial feedstock.	Early-stage R&D overseas, but poised to take off.	‘Green’ polyethylene could be produced in Victoria, to make non-biodegradable, recyclable plastics.
Ethylene carbonate	Important ‘green’ chemical industry feedstock and solvent in lithium-ion batteries.	Improved catalyst and reactor design for renewable feedstock being researched at Monash University.	Potential for domestic production of ‘green’ solvent for lithium-ion batteries. Research interest/expertise in Victoria to build upon.
Lignin-based polycarbonates & polyols	Versatile route to plant-based plastics, rubbers and adhesives.	Early-stage exploratory.	Potential to add value to lignin waste from Latrobe Valley papermaking plant.
Hydrogen-oxidising bacteria	Proteins for human and animal food.	Engineering R&D required to scale up a potentially explosive gas fermentation.	Potential for production of edible biomass/protein for aquafeed and human food products. Alternative to using biological conversion of syngas.

4.1.2 Brief Rationale for Prospective Technologies

4.1.2.1 Urea

Currently, Australia imports about 2.4 million t/y of urea, around 90 % of domestic demand. Even with the $6 billion Perdaman urea project under construction near Karratha WA, an opportunity will remain for another urea manufacturing facility on the east coast of Australia. VHI (formerly Latrobe Fertilisers) is currently working toward establishing a urea production plant in Victoria (Section 8.2.7.1).

The proposed HESC process is expected to produce 225,000 t/y hydrogen and 4.39 Mt/y CO_2 by-product (Kamiya et al. 2015). This amount of hydrogen could be converted to 1.56 Mt/y ammonia and then 2.7 Mt/y urea, consuming 1.8 Mt/y CO_2 in the process. Thus, producing ammonia from Victorian lignite would generate more CO_2 than needed for urea synthesis. In this case, **urea synthesis would consume about 41% of the waste CO_2, representing a major CO_2 recycling opportunity.**

Despite the fact that urea is the fertiliser of choice for Australian farmers, it is not the best option from an environmental perspective, because the incorporated CO_2 is eventually released back to the atmosphere. This could be partially mitigated by making ammonia using green hydrogen or blue hydrogen from co-gasification with biomass, or by reacting ammonia with biogenic CO_2. As suggested in Figure 11 above, the ammonia could also be converted into more environmentally-friendly fertilisers, such as ammonium sulphate or calcium ammonium nitrate.

4.1.2.2 Carbonation of concrete

Canadian company, CarbonCure Technology Inc. has patented a system for direct injection of CO_2 into fresh concrete during mixing, making it possible to carbonate large batches of concrete prior to forming. Validation trials established that the addition of CO_2 allowed a 7-8% reduction in the amount of cement used, without compromising the concrete strength or durability. The carbon intensity of the concrete is reduced by 6 - 8%, or 22.8 - 29.2 tonnes CO_2 benefit per tonne of CO_2 used. The Chicago Department of Transportation has allowed the use of CarbonCure technology in its infrastructure projects since June 2019. More than 2.5 million m^3 of concrete have been shipped with an estimated net savings of 36,000 tonnes of CO_2 (Section 7.1.3.1.4).

CarbonCure already has a presence in Australia, initially through Canberra-based Hi-Quality Concrete, and more recently through a partnership with BOC Gases. This technology is commercially available and easily deployable, and has the potential to make a significant contribution to reducing greenhouse gas emissions in Victoria if widely deployed in the construction industry and Government infrastructure projects.

ACI recommends that policymakers should assess whether there are any barriers, e.g., building standards, that would preclude the deployment of CarbonCure technology in Victoria. If not, then this should become part of standard practice. If barriers are identified, then Government-sanctioned trials should be undertaken to validate this process for inclusion in the relevant codes and standards.

4.1.2.3 Glasshouse horticulture

The use of CO_2 to boost crop productivity in glasshouses is a low volume, high value way to effectively recycle CO_2. While benefits are well known in the industry, the CO_2 is usually generated by burning fossil fuels within the glasshouse or by the direct injection of CO_2 from fossil sources. In the Netherlands, a joint venture between Linde Gas Benelux and VolkerWessels supplies over 400,000 t CO_2 from Shell's Pernis oil refinery to over 580 glasshouses via a pipeline distribution network (Section 6.1.1).

Glasshouse horticulture is an existing high value business in the Latrobe region. The development of a pipework network to convey recycled CO_2 to existing and new glasshouses would support the expansion of this valuable industry in the area, and provide employment opportunities at the low and medium skill levels for the Latrobe Valley community. A local glasshouse horticulturalist, Flavorite Tomatoes in Warragul, has previously expressed interest in exploring this opportunity.

There would be synergies in locating a new glasshouse complex close to a large CO_2 source in the Latrobe Valley, such as the proposed HESC lignite-to-hydrogen facility. Both CO_2 and waste heat could be beneficially used for crop production, and waste biomass at the end of the season could be co-gasified to reduce the emissions intensity of hydrogen production.

ACI recommends investigation of the feasibility of boosting the scale of glasshouse horticulture in this manner, in close proximity to the proposed HESC facility, to better understand the potential benefits for the Latrobe Valley community.

4.1.2.4 Supercritical CO_2 processing

The extraction of colours, oils and food extracts using supercritical CO_2 as a solvent is a well-established commercial process, although it is not well represented in Australia. Supercritical CO_2 processes, such as extraction, drying and extrusion, are low volume but high value and can produce high value food products and ingredients. In the textile industry, supercritical CO_2 dyeing is a new development which is rapidly being adopted by major brands because it is more efficient and environmentally-friendly (Section 5.2.1).

This technology could readily be established in Victoria to produce a range of specialist products for the food, nutraceuticals and cosmetics markets. An opportunity may exist for a specialised ingredient production business in Gippsland, adding value to the local agricultural industry and supporting the growth of new ventures, such as industrial hemp.

It is likely that a single supercritical CO_2 facility in the region could service a number of different business clients, and would benefit from a close association with Federation University in Churchill. **ACI recommends that a separate study be undertaken to investigate the business case for such an enterprise.**

4.1.2.5 Bipolar membrane electrodialysis (EDBM)

EDBM is a versatile commercial technology that is used to split simple salts into value-added acid and alkali byproducts. For example, with EDBM, renewable energy can split table salt (NaCl) into soda ash (NaOH) and hydrochloric acid (HCl). The NaOH can then be used to convert CO_2 into baking soda ($NaHCO_3$), useful commodity product (Section 7.4.1.4). Recent results from MIT indicate that baking soda can also be added to concrete mixtures, with a greater CO_2 reduction benefit than the CarbonCure technology (Section 7.1.3.1.5).

EDBM can potentially be employed in both renewables-powered DAC systems and processes for converting captured CO_2 into value-added products. The by-product acid stream could potentially be used to add value in other local industries. For example, sulphuric acid derived from sodium sulphate salt could be added to locally-produced ammonia to make ammonium sulphate fertiliser.

ACI suggests that EDBM should be regarded as a key enabling technology for new manufacturing opportunities in the Latrobe Valley, and recommends investigation for opportunities for its beneficial utilisation.

4.1.2.6 Carbonated fly ash

The four lignite-fired power stations in the Latrobe Valley (three still in operation) have collectively accumulated massive stockpiles of fly ash, which is stored as a valueless and hazardous waste in bunded retention ponds. Fly ash from the operation of Loy Yang A and B power stations would be of the order of 10 million tonnes, not to mention the ash from the Hazelwood and Yallourn power stations. In the context of CO_2 recycling, this intractable waste material is transformed into a highly valuable raw material. The fly ash contains calcium and magnesium, which will react with CO_2 to form a deposit of carbonate that passivates the surface and makes the fly ash non-hazardous.

Carbonated fly ash can be used as a ‘supplementary cementitious material’ in concrete, where it improves the workability of wet concrete, and increases its strength and durability. It is a simple, cost-effective way to reduce the emissions intensity of concrete, with great potential significance because of the huge quantities available (Section 7.1.2.3).

Previous research at the University of Wyoming (the SequestTech process, Section 7.1.2.3.1) has demonstrated the successful carbonation of fly ash at pilot scale (TRL 6). In the United Kingdom, Carbon8 Systems (Section 7.1.1.3) has developed a carbonation-granulation system with TRL of 8 – 9. Currently Latrobe Magnesium (Section 7.1.2.3.2) is building a pilot plant to extract elemental magnesium from Hazelwood fly ash. This is an example for other entrepreneurs to follow in Victoria, extracting value from an otherwise valueless waste material.

ACI recommends that research on fly ash carbonation be undertaken at a scale sufficient to produce samples for safety and performance assessment, market development, and regulatory approval for use as a construction material.

4.1.2.7 Calcium/Magnesium carbonate

Research at Monash University has shown that the calcium and magnesium ions in fly ash can be extracted with a benign, regenerable solvent and then reacted with CO_2 to form calcium and magnesium carbonates (Section 7.2.2). In the United States, Blue Planet (Section 7.1.1.2) has patented this approach (but not in Australia), and using it to produce a carbon-negative construction material. Precipitated calcium carbonate (PCC) is used commercially as a filler in plastics, paints, concrete and composite materials, and in papermaking. Precipitated magnesium carbonate can be used to produce a lightweight, insulating plasterboard that is water resistant, non-toxic, and fire-proof, with the ability to be cut and fastened using conventional methods.

Both Calera/Fortera (Section 7.1.1.1) and Carbon Capture Machine (Section 7.3.1.1) are actively developing products based on calcium and magnesium carbonates, but there appears to be scope for development of new business opportunities based on inorganic carbonation of Latrobe Valley fly ash.

ACI recommends that a patent search be undertaken to determine the freedom to operate in this space. It also recommends that the Monash University process should be further developed to pilot scale (TRL 6), so that samples of calcium and magnesium carbonate can be produced for product development and market evaluation.

In addition, it is also recommended that a fundamental study be undertaken to quantify the Rare Earth Elements present in lignite fly ash, if any, to clarify whether there may be an opportunity to recover REEs as another valuable product.

4.1.2.8 Syngas by Solid Oxide Electrolysis (SOE)

Syngas (synthesis gas, predominantly carbon monoxide and hydrogen) is a commonly used feedstock for production of chemicals and liquid fuels. Syngas can most economically be made by large-scale reforming of natural gas or gasification of lignite, but the focus here is on recycling CO_2 using renewable hydrogen.

There is great international interest in the use of renewable energy to convert CO_2 to useful chemicals and fuels. Danish company Topsøe's has developed the eREACT™ reverse-water-gas-shift reactor system to produce syngas from CO_2 and H_2 (Section 8.3.4.1.2). German company Sunfire GmbH has commercialised a process for producing syngas by high temperature SOE co-electrolysis of steam and CO_2 (Section 9.2.1.1.1).

In Victoria, a CSIRO-led consortium is also developing a SOE-based process (Section 9.2.1.2). The CSIRO group in Clayton has considerable expertise in this field, with an excellent facility and technical capabilities, and a solid track record in commercialising its research outputs.

The SOE technology can be employed in two different ways. One is for production of syngas for catalytic conversion of CO_2 to useful chemicals and fuels, such as methane and methanol. The second is for production of ethanol using LanzaTech's gas fermentation process (Section 6.3.2.1.1). This is likely to be a more economical route to ethanol production, compared with syngas production by gasification, which requires high throughput to achieve economies of scale.

ACI recommends support for further development and scale up of this technology to TRL 6 and beyond, to serve as a platform for the development of higher value products such as methane, methanol and ethanol.

4.1.2.9 Methanol by catalysis

Methanol is one of the most important commodities in the chemical industry, and is actively being being developed as a hydrogen carrier fuel for the shipping industry. Europe's largest green e-methanol facility, FlagshipONE, is expected to enter into operation in 2025 and will produce around 50,000 tonnes of e-methanol each year, and other major e-methanol projects are under development. These processes are based on Topsøe's eREACT™ system, which produces syngas from CO_2 and green hydrogen, and methanol by conventional hydrogenation of CO (Section 8.3.5.1.1.2).

Methanol can also be synthesised by hydrogenation of CO_2 at high temperature and pressure using commercial catalysts. Mitsui Chemicals, Carbon Recycling International and BSE Engineering have successfully demonstrated this process at industrial pilot scale (Section 8.3.5.1.2). Hence this is a relatively mature technology, with a TRL of 7 – 8. However, in most instances this process will not be cost-competitive with existing fossil-derived methanol, so it necessary to develop more effective catalysts and systems so that it can proceed under milder operating conditions.

Techno-economic studies of methanol synthesis have suggested that an inexpensive source of CO_2-free hydrogen is essential, and the poor process economics could be improved by upgrading methanol to higher-value derivatives such as dimethyl carbonate (DMC) and dimethyl ether (DME).

In Victoria, CSIRO is working on integration of catalytic hydrogenation into the CO_2 capture process, with the aim of eliminating the costs involved in CO_2 recovery, purification and compression (Section 8.3.5.2.1). The University of Melbourne has a portfolio of projects aimed at developing new catalyst and reactor systems to allow the CO_2 hydrogenation reaction to proceed under milder conditions (Section 8.3.5.2.2). In addition, Monash University has expertise in catalyst design for production of DMC and DME.

Due to value of methanol as a key product and intermediary in a low emissions economy, ACI recommends that the research expertise in Victoria be supported to further develop and scale up this technology.

4.1.2.10 Ethanol by catalysis

Apart from its use as a fuel, ethanol is also a promising hydrogen carrier and a versatile building-block for chemicals, fuels and polymers. One of the most prospective uses for renewable ethanol is for conversion to ethylene, which is a very important chemical industry feedstock, including as a precursor for polyethylene (as produced by Qenos in Altona). Dehydration of ethanol to ethylene is a well-established technology that is commercially available, but catalytic conversion of CO_2 to ethanol is not yet sufficiently selective or efficient. The traditional candidate catalysts tend to produce CH_4 or CO as co-products, so great efforts have been expended to identify new catalyst compositions and configurations (Section 8.3.6).

While the catalysts required for hydrogenation of CO_2 to ethanol are currently at TRL 2-3, they have the potential to be scaled up and commercialised very quickly once an optimal formulation has been identified. Given that Qenos is the largest manufacturer of polyethylene in Australia, and its feedstock for ethylene synthesis is dependent on dwindling supply from Bass Strait, ACI considers that local R&D on production of industrial ethanol is of vital strategic importance to the manufacturing industry in Victoria and Australia.

ACI recommends support for research in Victoria on efficient catalysts for conversion of CO_2 to ethanol, so as to be well positioned to capitalise on any breakthroughs, either locally or internationally.

4.1.2.11 Ethylene carbonate (EC)

Ethylene carbonate is a cyclic organic carbonate, widely used as a solvent, industrial lubricant, precursors for polycarbonate synthesis, and electrolyte for lithium-ion batteries. The growing demand for electric vehicles is driving growth in the global market for EC, but the current industrial process for EC synthesis involves reaction of CO_2 with ethylene oxide, which is a toxic petrochemical (Section 8.1.3.3).

Research is currently under way at Monash University to develop a novel catalytic reaction system for synthesis of EC from renewable feedstock, which should be of commercial interest. This research s novel and at the forefront of international research in this field. Given the growing demand for use of EC in lithium-ion batteries, and the desirability of using renewable feedstocks, **ACI recommends continued research toward scale-up of this technology.**

4.1.2.12 Lignin-based Polyurethane

Polyurethanes, with a global production of about 20 million tonnes in 2014 are among the top six most extensively used polymers. They are used in practically all fields of polymer applications – foams, elastomers, thermoplastics, thermorigids, adhesives, coatings, sealants, fibres, etc. Polyurethanes incorporating recycled CO_2 are now being produced commercially by reacting polycarbonate polyols with isocyanate. However, safer biological alternatives are being sought for both the polyol and isocyanate components, to produce bio-based non-isocyanate polyurethanes.

An approach with great potential is to use lignin, a waste product from paper-making, as a feedstock for eco-friendly polyurethanes, along with organic carbonates made from recycled CO_2 (Section 8.1.4.1.3.1). Research on this topic is at an early stage, with no known activity in Victoria, but the opportunity to produce a 'green' version of a major commodity polymer in Victoria is of significant interest and potential. **An independent review of this topic is recommended, to determine the extent of the opportunity and the investment required.**

4.1.2.13 Hydrogen-oxidising bacteria

Gas fermentation of the hydrogen-oxidising bacterium *Cupriavidus necator*, which grows on oxygen, hydrogen and CO_2, had its origins in a 1960s NASA-funded program to develop a life-support system for astronauts in space. Currently, two companies in the United States, NovoNutrients and Kiverdi, are developing processes utilising hydrogen-oxidising bacteria to convert CO_2 into microbial biomass for use as animal and human foods. The same approach is being pursued by Solar Foods in Finland (Section 6.3.3).

These companies are working to meet the growing world demand for a protein-rich diet, which cannot sustainably be supported through agricultural means alone. The biomass from hydrogen-oxidising bacteria can be processed into high quality protein, which can be further upgraded to a variety of food products, for both human and animal consumption. Using this process to convert waste CO_2 into valuable food products would seem to have huge potential.

Although there is currently no research being undertaken on hydrogen-oxidising bacteria production in Victoria or Australia, ACI recommends this as a topic worthy of further investigation.

4.1.3 Timeframe for Commercialisation

To help bring the identified opportunities into perspective, Figure 12 below ranks the prospective technologies according to their Technology Readiness Level (defined in Appendix 2).

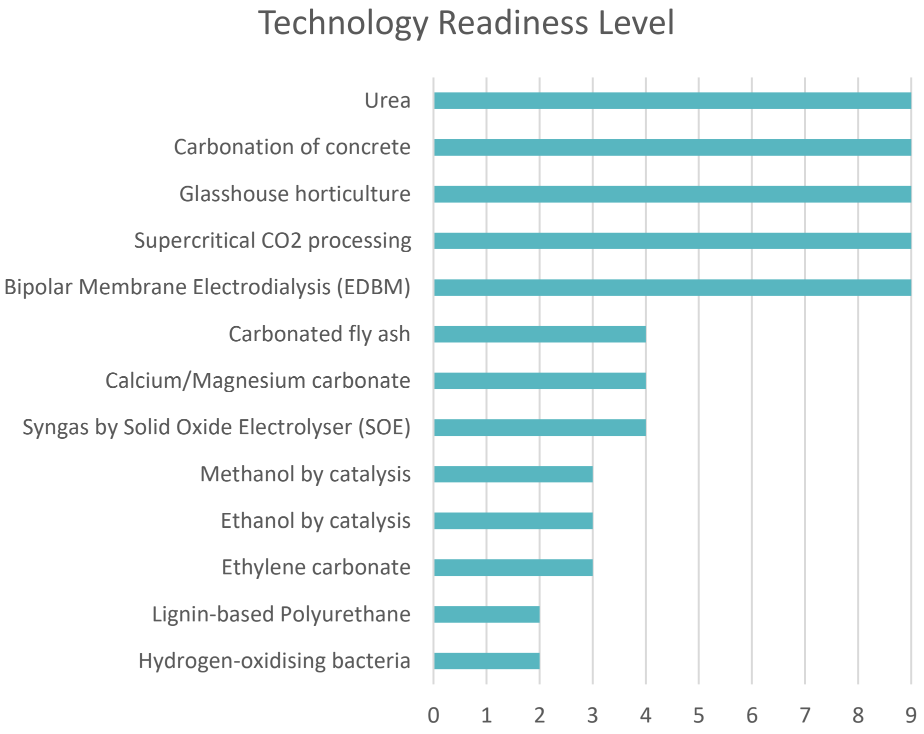

Figure 12: *Development status of prospective CO_2 recycling opportunities*

Five of the technologies are at TRL 9, and are ready for immediate commercialisation if a business case can be made. The others are ranked at TRL 4 or lower in the Victorian context, even though they may be further developed overseas. They are regarded as prospective for Victoria, but work is needed to develop them up to pilot scale and beyond in Victoria.

This will take time, which is dependent on whether or not there is already relevant research expertise in Victoria that can be leveraged. ACI's assessment on whether the processes can be developed locally in the short-, intermediate- or long-term is shown in Figure 13 below.

	SHORT-TERM	INTERMEDIATE	LONG-TERM
TRL 1-3			Ethanol Ethylene Carbonate Lignin-based Polyurethane H_2-oxidising bacteria
TRL 4-6		Carbonated Fly Ash Ca/Mg Carbonates Methanol Syngas by SOE EDBM	
TRL 7-9	Concrete Carbonation Glasshouse Horticulture S-CO_2 Processing	Urea	

Figure 13: *Timeframe for commercialisation of prospective* CO_2 *recycling opportunities*

The short-term opportunities represent the least complicated uses for CO_2, while the other options require active research to develop their potential. Commercial equipment is available for urea production, but this has a longer timeframe than the direct uses of CO_2. Fortunately, an existing research skills base is available in Victoria to support this technology development pathway, and work is already occurring on some of the nominated technologies.

4.1.4 Comparison with Previous Reviews

The selection of prospective CO_2 recycling technologies is broadly consistent with the findings from previous reviews, with an additional emphasis on supporting and developing local research expertise to build the skills needed for commercialisation in Victoria.

Previous reviewers also identified direct use of CO_2 (glasshouses, supercritical CO_2) and carbonation of concrete as having the shortest time to commercialisation (Alberici et al. 2017; Pan et al. 2018; Srinivasan et al. 2021). Mineral carbonation (e.g., carbonation of concrete and fly ash) is considered to have the greatest carbon abatement potential (Alberici et al. 2017; IEA 2019; IEAGHG 2021), but the speed at which they can be deployed is limited by building codes and standards that are based on composition, not performance (IEA 2019; IEAGHG 2021; Li et al. 2022).

Fuels (e.g., methanol, ethanol) have great potential due to their vast market size (IEA 2019; IEAGHG 2021), but the cost is too high (Alberici et al. 2017). Urea, calcium/magnesium/sodium carbonates, and syngas also have significant market volume, while organic carbonates (e.g., ethylene carbonate) are low-volume high-value (Chauvy et al. 2019). However, CO_2-based chemicals and fuels are considerably more expensive than conventional fossil-based products (IEAGHG 2021), justifying research in improved catalysts and processes to bring down costs.

The technology selection presented here is also consistent with CSIRO's *'CO_2 Utilisation Roadmap',* which suggests that applications for captured CO_2 will progress from direct use in the short-term to progressive demonstrations and commercialisation of mineral carbonation, chemicals and fuels, followed in the longer-term by biological processes (Srinivasan et al. 2021).

The concept presented here, of an industrial ecosystem playing to the strength of the natural resources available in the Latrobe Valley, is also consistent with CSIRO's recommendation to deploy CO_2 recycling technologies to leverage infrastructure that already exists or is planned for construction (Srinivasan et al. 2021).

While the identified CO_2 recycling opportunities are broadly aligned with the findings of previous reviewers, they also reflect the unique resources available in Victoria, in terms of natural resources, commercial interests, and existing research activities. Together, these have potential to be channeled toward the creation of new, green manufacturing jobs in Victoria. New CO_2-based industries would provide employment in skilled, high paid, interesting jobs, making the Latrobe Valley a more desirable place to live and work.

4.1.5 Key Recommendations Arising

The selection of CO_2 recycling technologies highlighted in this report is based on recommendations that are scattered throughout this report. The topic of CO_2 recycling is so large and complex, with so many ancillary side-topics, that it is difficult to effectively summarise without losing detail. To assist the reader, all the recommendations throughout the report are collated in Section 4.1.6 following.

A key finding of this report is that a variety of technologies for inorganic carbonation have already passed through the R&D phase and been successfully commercialised overseas. CarbonCure has standardised its system for injection of CO_2 into concrete slurry and sold more than 650 units in thirty countries, producing about 5 million truckloads of low-carbon concrete. Systems for producing low-carbon concrete blocks, slabs, pavers and tiles have been commercialised by Solidia, Carbicrete, CarbonBuilt. Carbon8 Systems has commercialised its process for direct carbonation of solid wastes, and Blue Planet has commercialised its process for continuous extraction of Ca/Mg from solids and precipitation as Ca/Mg carbonates. CarbonFree has commercialised its process for producing baking soda using hydroxide extracted from low-cost salts.

This is significant, because these represent high-volume low-value markets that can achieve significant CO_2 emission reductions, mostly for the construction sector, including concrete formwork, pre-formed concrete blocks, slabs, etc., insulation and plasterboard. This is an ideal way to foster a low-emissions economy, because the captured CO_2 is permanently sequestered into valuable products in a sector that is large and continually growing.

As such, inorganic carbonation is an area of R&D that urgently needs to be kick-started in Australia. Coordinated research by both industry and academia is required, supported by policy direction from the government. The scale of the opportunity is significant, with Victoria using around 16 million tonnes of cementitious product each year. Reducing the associated GHG emissions, and preferably reaching net-negative, is essential for the state to meet its net zero by 2045 target.

Victoria is well placed to capitalise on this opportunity. The power stations in the Latrobe Valley have produced tens of millions of tonnes of Ca/Mg-rich fly ash, which could be upgraded by carbonation into a supplementary cementitious material, creating a new revenue stream for the power companies. The fly ash could be further value-added by solubilising the Ca/Mg components for reaction with CO_2 or sodium bicarbonate, with possible separation of the Ca and Mg components, to produce Ca, Mg or Ca/Mg carbonates as individual products.

Moreover, the processes involved in inorganic carbonation are also directly applicable to direct air capture (DAC) of CO_2, which will also need to expand rapidly in the near future. There are presently 19 DAC plants operating worldwide, capturing only around 0.01 Mt CO_2/year (Ozkan et al. 2022). Most DAC systems capture CO_2 using aqueous solutions of potassium hydroxide or sodium hydroxide, but regenerating the alkali requires high temperatures (> 900 ^{o}C) and are energy-intensive (Sodiq et al. 2023). There would appear to be opportunities to integrate some of the inorganic carbonation technologies with DAC, to simultaneously capture CO_2 and transform it into valuable Ca/Mg carbonate products for the construction industry. This would create an economic incentive for DAC and couple its growth to the burgeoning construction sector.

The only concrete carbonation technology currently available in Australia is the CarbonCure CO_2 injection system, which was first licensed by an ACT concrete producer and is now available in Victoria through BOC Gases. This technology is commercially available and easily deployable, and has the potential to make a significant contribution to reducing GHG emissions in Victoria if widely deployed in the construction industry and Government infrastructure projects.

ACI recommends that policymakers assess whether there are any barriers, e.g., building standards, that would preclude the deployment of CarbonCure technology in Victoria. If not, then this should become part of standard practice and mandated for all new infrastructure projects. If barriers are identified, then Government-sanctioned trials should be undertaken to validate this process for inclusion in the relevant codes and standards. The Victorian Government could also provide essential support through public procurement of low-carbon products with verifiable climate benefits, and incentives for the public and private sectors to invest in and consume these products. The “Big Build” initiative is a once-in-a-generation opportunity to demonstrate innovation in the materials procurement process for Victoria.

This study has also identified, for the first time, that three water treatments plants in the Melbourne metropolitan area (Western, Eastern and Yarra Valley) collectively produce about 100,000 t/y CO_2 which, if captured and stored, would qualify as carbon-negative emissions. CO_2 capture systems suited to this scale of operation are commercially available, prefabricated for easy installation (Section 5.1.2.2). Injection of this biogenic CO_2 into concrete would significantly help the construction sector reduce its greenhouse gas emissions.

Of course, the immediate response to this suggestion is that it is no financial reason to do this, because the CO_2 emitted from biogas is carbon-neutral. This type of thinking is past its use-by date. Biogenic CO_2 that is captured and either permanently stored or converted into long-lived manufactured goods is carbon-negative, and thus should be eligible for carbon credits. This provides an opportunity to monetise the CO_2 that is currently allowed to go to waste. In the net-negative mentality that we must adopt, all CO_2 emissions to the atmosphere contribute to global warming and must be reduced. **ACI recommends that a study be undertaken to investigate the issues and likely costs involved in implanting CO_2 capture at municipal water plants, identify any policy barriers that need to be addressed, and identify or suggest possible incentives that could assist in bringing this to reality.**

Also, Boral's Blue Circle Southern cement works in Waurn Ponds produces cement kiln dust as a by-product. Modular CO_2 capture systems are now available (e.g., Carbon Clean[17], Aker Carbon Capture[18], Mitsubishi Heavy Industries[19]) that could be used to capture CO_2 emissions from the kiln flue gas for carbonation of the kiln dust. This combination would make the cement from Blue Circle Southern close to carbon neutral. **ACI recommends that this option be included in the above study.**

The second short-term opportunity identified in this study, use of CO_2 in glasshouse horticulture, represents a potential customer for CO_2 captured from water treatment biogas. There are existing glasshouse horticulture businesses in Victoria which rely on gas burners to generate CO_2, and require alternatives to help transition away from natural gas use. Overseas, CO_2 from biogas is trucked or piped to glasshouse horticulture facilities. In principle, there is no reason why this could not be done in Victoria. **ACI recommends that a study be undertaken to engage with Victorian glasshouse horticulturalists and investigate the potential business case for using captured biogenic CO_2 to enhance crop production.**

The third short-term opportunity identified in this study, supercritical CO_2 (S-CO_2) processing, is commercially available technology but has no local business uptake. This is an instance where a pilot-scale development facility would encourage local entrepreneurship and development of new business opportunities. Federation University in Churchill would be an ideal location for such a facility, to encourage monetisation of existing and new plant crops, producing new food and pharmaceutical ingredients. **ACI recommends that a study be undertaken to develop a business plan for such an R&D facility at Federation University.**

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[17] https://www.carbonclean.com/modular-carbon-capture-systems
[18] https://akercarboncapture.com
[19] https://www.mhi.com/products/engineering/co2plants_process.html

Production of urea is listed as an intermediate-term opportunity in Victoria, even though it is an established commercial process. This is because it is secondary technology, being dependent on commercial availability of sufficient quantities of hydrogen (green or blue) and CO_2 (fossil or biogenic). Over time, increasing demand from Japan for hydrogen and ammonia as clean fuels will stimulate investment in both hydrogen and ammonia production in Victoria, predominantly from lignite but supplemented by renewable energy and biomass. Establishment of these capabilities is likely to be a necessary precursor for urea production in Victoria. As is done elsewhere, the balance of production could be shifted between ammonia and urea in response to market demand and relative prices, to maximise profitability. **ACI recommends continued development of skills in industrial pilot scale gasification of lignite and biomass, and the associated skills in CO_2 capture and processing and hydrogen processing.**

The other opportunities placed in the intermediate-term category (carbonated fly ash, calcium/magnesium carbonates, methanol, syngas by SOE, EDBM) are not yet ready for commercialisation in Victoria. In some cases, appropriate technologies have been developed overseas and could potentially be utilised in Victoria, e.g., Carbon8 Systems, Blue Planet, or could be adapted from other industries, e.g., EDBM. Some are being investigated by local researchers. However, in the absence of support from government and the community, these opportunities will not materialise.

The opportunities placed in the long-term category (ethanol, ethylene carbonate, lignin-based polyurethane, H_2-oxising bacteria) are seen as having potential to be the basis for new manufacturing industries in Victoria, including green fuels, plastics and food ingredients. These require further research at lab scale and then scale-up, and currently lack any industrial support. Research is also required on development of compact solar thermal heat storage systems, to provide the high temperatures (~600 ^oC) needed to overcome the energy barrier of CO_2 conversion. **ACI recommends that government funding be allocated to support strategic research to underpin the creation of these new manufacturing industries in Victoria.**

Beyond this, there are likely to be opportunities for conversion of CO_2 into high-value low-volume fine chemicals, but these are beyond the scope of this report. **ACI recommends that an independent review of developments in this area be undertaken by a qualified expert, to provide guidance on the opportunities that exist for strategic research efforts.** This review should include detailed consultations with representatives of the relevant chemicals and plastics industries.

Given the urgency with which the climate change emergency must be addressed, new thinking is required on how to stimulate and support the development, demonstration and commercialisation of CO_2 capture and recycle technologies in Australia. In the absence of any kind of pricing mechanism that reflects the value to society of CO_2 capture and recycle, market forces alone will not deliver the necessary outcomes.

This situation is not isolated to Victoria alone. Previous reviews have identified it as being a common challenge as the world grapples with the implications of climate change. It is broadly understood that CO_2 recycling technologies can only be successfully introduced if they are seen as desirable and are actively supported and coordinated at all levels – policy, industry and public. To this end, it is worth repeating the **key recommendations made by previous reviewers**:

- Early opportunities, such as the use of CO_2 in building materials, can be stimulated through Government support for product testing trials and updating of standards, and through public procurement of low-carbon products with verifiable climate benefits (IEA 2019), further supported by incentives for the public and private sectors to invest in and consume these products (IEAGHG 2021; Li et al. 2022).
- Financial incentives and mechanisms are needed to accelerate investment in CO_2 recycling technology research and development, as well as demonstration at the scale needed to attract further investment (Alberici et al. 2017; IEAGHG 2021; Srinivasan et al. 2021).
- Support mechanisms are needed that allow CO_2 recycling to receive recognition for sustainability benefits and compete on a more level-playing field with conventional products (IEAGHG 2021), including integration with existing strategies and green mechanisms (Srinivasan et al. 2021).
- Awareness of CO_2 recycling and its role in the decarbonisation challenge needs to be raised within government, the private sector and the wider public (Alberici et al. 2017; Srinivasan et al. 2021).
- At the same time, public awareness needs to be raised of the life cycle emissions associated with existing fossil-based products, highlighting the changes that individuals can bring about through their collective choices (IEAGHG 2021).
- A piecemeal approach will not be successful. Engagement and close collaboration between all interested parties is required (Srinivasan et al. 2021), and knowledge transfer must be facilitated (Alberici et al. 2017).

An additional issue faced by technology developers in Australia is that there are insufficient support mechanisms to help bridge the “chasm of death” between laboratory research and pre-commercial demonstration. A new approach is needed.

An approach that has worked before, in the United States, is to offer a cash incentive to encourage technology developers to engage with large industry and private philanthropists for financial support. The NRG COSIA Carbon XPRIZE was a five-year global competition (2015-2020) offering US$20 million prize money for development of breakthrough technologies to convert CO_2 into high value products. It was supported by major commercial sponsors that provided the prize purse and operational funding, as well as contributing mentorship and industry knowledge.[20] This approach was clearly successful, because the two joint winners, CarbonCure and CarbonBuilt, were successfully commercialised with the aid of the support and high public profile they received.

A similar approach could work in Victoria, but it would require coordination. It is suggested that ACI is ideally positioned to take on this role. ACI is a not-for-profit organisation that has managed a R&D project portfolio worth more than $60 million on behalf of the Victorian and Australian governments. It

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[20] https://www.xprize.org/prizes/carbon/sponsors

has been one of the largest sponsors of CO_2 capture research in Australia, and has a good working relationship with all the relevant researchers in Victoria. Importantly, ACI does not seek a stake of any of the intellectual property developed in the projects it manages, allowing it to act as a trusted broker of research partnerships.

It is suggested that ACI could coordinate a competition to kick-start significant commercial development of CO_2 recycling (including DAC) in Victoria, drawing upon corporate sponsorship and relevant international commercial interests (e.g., CarbonCure, Carbon8 Systems, etc.) to partner with local researchers and entrepreneurs. This would quickly highlight the potential of CO_2 recycling in Victoria, and start the conversations needed to address the issues and concerns that will inevitably be raised.

To further develop this concept, **it is recommended that a follow-up scoping study be undertaken by ACI, to develop a detailed plan setting out how a competition of this nature might be set up and run**. A working group of interested parties should be established to oversee this process, including representatives of relevant State government departments, to ensure that any regulatory hurdles are identified and addressed.

4.1.6 Summary Table of Recommendations Made Throughout Report

Recommendation	Report Reference
Previous Reviews	
Early opportunities, such as the use of CO_2 in building materials, can be stimulated through Government support for product testing trials and updating of standards, and through public procurement of low-carbon products with verifiable climate benefits, further supported by incentives for the public and private sectors to invest in and consume these products.	Section 3.1
Financial incentives and other market mechanisms are needed to accelerate investment in CO_2 recycling technology R&D, as well as demonstration at the scale needed to attract further investment. Traditionally only grants have been used to encourage R&D, however these are often limited, of low value and do not have a bridging mechanism as the technology develops. Government should consider equity funding, debt funding, low-cost loan facilities and stepped grant programs whereby further funding is provided based on the success of earlier phases of the research, up to and including demonstration.	Section 3.1
Support mechanisms are needed that allow CO_2 recycling to receive recognition for sustainability benefits and compete on a more level-playing field with conventional products, including integration with existing strategies and green mechanisms.	Section 3.1
Awareness of CO_2 recycling and its role in the decarbonisation challenge needs to be raised within government, the private sector and the wider public.	Section 3.1
Public awareness needs to be raised of the life cycle emissions associated with existing fossil-based products, highlighting the changes that individuals can bring about through their collective choices.	Section 3.1
A piecemeal approach will not be successful. Engagement and close collaboration between all interested parties is required, and knowledge transfer must be facilitated.	Section 3.1
ACI Recommendations	
ACI recommends that policymakers should assess whether there are any barriers, e.g., building standards, that would preclude the deployment of CarbonCure concrete carbonation technology in Victoria. If not, then this should become part of standard practice. If barriers are identified, then Government-sanctioned trials should be undertaken to validate this process for inclusion in the relevant codes and standards.	Section 4.1.2.2
ACI recommends that research on fly ash carbonation be undertaken at a scale sufficient to produce samples for safety and performance assessment, market development, and regulatory approval for use as a construction material.	Section 4.1.2.6
ACI recommends that a fundamental study be undertaken to quantify the Rare Earth Elements present in lignite fly ash, if any, to clarify whether there may be an opportunity to recover REEs as another valuable product.	Section 4.1.2.7

It is suggested that ACI could coordinate a competition to kick-start significant commercial development of CO_2 recycling (including DAC) in Victoria, drawing upon corporate sponsorship and relevant international commercial interests to partner with local researchers and entrepreneurs. It is recommended that a follow-up scoping study be undertaken by ACI, to develop a detailed plan setting out how a competition of this nature might be set up and run.	Section 4.1.5
ACI recommends that priority should also be given to research on development of more efficient renewable energy systems, to produce the electricity needed to drive the low-emissions processes of the future.	Section 4.1.5
ACI recommends that priority should also be given to research on development of compact solar thermal heat storage systems, to provide the high temperatures (~600 °C) needed to overcome the energy barrier of CO_2 conversion.	Section 4.1.5
Supercritical CO_2 extraction is a high value, low volume process that could readily be established in Victoria to produce a range of specialist products for the food, nutraceuticals and cosmetics markets. It is likely that a single supercritical CO_2 facility in the region could service a number of different business clients, and would benefit from a close association with Federation University in Churchill. ACI recommends that a separate study be undertaken to investigate the business case for such an enterprise. Victoria has one local textile dyeing company, Geelong Dyeing, which is well positioned to take advantage of the DyeCoo process.	Section 5.2.1.8
The scale of industrial hemp cultivation should be increased in Victoria. Hemp can be grown to produce fibre for construction purposes, feedstock for bioenergy and hydrogen, and seed for functional foods, oils, cosmetics, personal care, and pharmaceuticals.	Section 5.2.1.8
An opportunity may exist for a specialised ingredient production business in the Latrobe Valley, drawing upon the agricultural products produced in the region as well as specialised products such as Australian native foods. A separate study is recommended to examine the business case for such an enterprise.	Section 5.2.1.8
Glasshouse horticulture is an existing high value business in the Latrobe region. The use of CO_2 to boost crop productivity in glasshouses is a low volume, high value way to effectively recycle CO_2. The development of a pipework network to convey recycled CO_2 to existing and new glasshouses would support the expansion of this valuable industry in the area. Additionally, greenhouses are labour intensive and would provide significant employment opportunities at the low and medium skill levels for the Latrobe Valley community.	Section 6.1.2
There is a growing world demand for a protein-rich diet, which cannot sustainably be supported through agricultural means alone. The biomass from hydrogen-oxidising bacteria can be processed into high quality protein, which could be further upgraded to a variety of food products, for both human and animal consumption. Using this process to convert waste CO_2 into valuable food products would seem to have huge potential, and is worthy of further investigation.	Section 6.3.3.3

Carbonation of fly ash with recycled CO_2 has the potential to convert a problematic waste into a new type of construction material. Carbonated fly ash has been recommended for use as a partial replacement for cement in concrete on the basis of its cost-effectiveness, ease of processing and greenhouse gas credentials. Victoria should actively investigate the inclusion of carbonated fly ash in the specification of concrete in the construction industry.	Section 7.1.2.6
The process of direct injection of CO_2 into fresh concrete, under development by CarbonCure Technology, is technically viable and a proven way to reduce the CO_2 footprint of concrete products. CarbonCure has recently partnered with BOC to facilitate deployment of the technology in Australia. As such, this is a technology that can be adopted immediately.	Section 7.1.3.3
The potential for addition of baking soda during concrete production should be a high priority for research in Victoria. MIT researchers found that sodium bicarbonate can substitute for 20% of Portland cement in a concrete mix, and reduce overall CO_2 concrete emissions by 15%. If this can be validated through concrete performance trials, this would be the single largest opportunity for CO_2 recycle identified in this report.	Sections 7.1.3.3 and 7.4.2
There is an opportunity for local development of the Monash University / Blue Planet mineralisation process, to add value to the vast stockpile of fly ash in the Latrobe Valley through production of precipitated calcium carbonate and magnesium carbonate. ACI recommends that a patent search be undertaken to determine the freedom to operate in this space.	Section 7.2.3
The Monash University / Blue Planet mineralisation process could also be used to produce magnesium carbonate from fly ash, for manufacture of fire-resistant construction boards. ACI recommends that the Monash University process should be further developed to pilot scale (TRL 6), so that samples can be produced for product development and market evaluation.	Section 7.3.3
EDBM can potentially be employed in both renewables-powered DAC systems and processes for converting captured CO_2 into value-added products. EDBM membranes can produce NaOH from table salt and renewable energy, which could underpin a new industry sector based on upgrading fly ash with captured CO_2. The EDBM process is a key enabling technology for new manufacturing opportunities and DAC in the Latrobe Valley, so opportunities for its deployment should be investigated.	Section 7.4.2
Inorganic carbonation is an area of R&D that urgently needs to be kick-started in Australia. Coordinated research by both industry and academia is required, supported by policy direction from the government. It is recommended that this be undertaken as a matter of high priority.	Section 7.5
The research on ethylene carbonate synthesis at Monash University is novel and at the forefront of international research in this field. Given the growing demand for its use in lithium-ion batteries, and the desirability of using renewable feedstocks, continued research toward scale-up of this technology is recommended.	Section 8.1.3.4

The chemistry of polycarbonate polymers and polyols is very versatile and represents a new and very important avenue for conversion of CO_2 into value-added products, particularly those based on waste lignin. Waste lignin is produced in large quantities in the Latrobe Valley, at the Australian Paper papermaking plant at Maryvale. The possibility of producing a major commodity polymer in Victoria from lignin and CO_2 is of significant interest and potential. An independent review of this topic is recommended, to determine the extent of the opportunity and the investment required.	Section 8.1.4.3
There is potential for a urea manufacturing facility in the Latrobe Valley, producing for both the domestic and export markets. Urea synthesis would consume about 41% of the CO_2 generated in ammonia production, representing a major CO_2 recycling opportunity.	Section 8.2.9
There are opportunities for conversion of CO_2 into high-value low-volume fine chemicals. ACI recommends that an independent review of developments in this area be undertaken by a qualified expert, to provide guidance on the opportunities that exist for strategic research efforts. This review should include detailed consultations with representatives of the relevant chemicals and plastics industries.	Section 8.2.9
Victorian research on lignite gasification laid the groundwork for and supported the successful HESC pilot project. Technical options exist to make gasification with CCS net zero emissions, or even net negative. ACI recommends further support for gasification R&D, to better understand the implications of biomass gasification and to create local skills in the emerging hydrogen economy.	Section 8.3.3.3
Methanol is a key product and intermediary, so research on more cost-effective synthesis and upgrading routes is obligatory. Research is already occurring in Victoria, which should be supported and expanded.	Sections 8.3.5.3 and 8.3.7.3
Alternative routes for production of ethanol, as a fuel and feedstock for chemical conversion (e.g., to ethylene), are of immense commercial significance. The future of polyethylene production at the Qenos Altona plant is jeopardised by declining output from the Bass Strait gas fields, so local R&D on production of industrial ethanol via syngas conversion or hydrogenation of CO_2 is of vital strategic importance to the manufacturing industry in Victoria and Australia. ACI recommends support for research in Victoria on efficient catalysts for conversion of CO_2 to ethanol, so as to be well positioned to capitalise on any breakthroughs, either locally or internationally.	Section 8.3.6.3
Catalytic reduction of CO_2 using Solid Oxide Electrolyser (SOE) technology is the most prospective approach for upgrading renewable energy to valuable chemicals. CSIRO currently has a range of projects under development around Solid Oxide Electrolyser technology, produce syngas and further upgrading to methane, methanol, fuels, etc. ACI recommends support for further development and scale up of this technology to TRL 6 and beyond, to serve as a platform for the development of higher value products such as methane, methanol and ethanol.	Section 9.2.1.3

5 Direct Use of CO_2

5.1 CURRENT APPLICATIONS FOR CO_2

5.1.1 Availability of CO_2 in Australia

Carbon dioxide is a well-known industrial gas with a long history of use. It is most widely employed in the carbonation of beverages, to give the fizz to soft drinks. It is also utilised to provide a blanket of inert gas in welding and in the food industry, and as a fire retardant in fire extinguishers. In frozen form, as ‘dry ice’, it is a cooling medium and as an industrial ‘dry ice blasting’ cleaning. These well-established applications are based on the physical properties of CO_2 and do not involve any chemical modifications.

It is difficult to find reliable information on the quantities of CO_2 used in these applications, as it is not usually publicly disclosed. Naims (2016) provided estimates for global CO_2 consumption, as shown in Table 5 below.

***Table 5**: Current and near-term markets for products utilising CO_2 (Naims 2016)*

Product/application	Current est. volumes CO_2, kt/y
Beverage carbonation	2900
Food packaging	8200
Industrial gas	6300
Oil and gas recovery	25,000
Total	**42,400**

In Australia, the revenue generated by the CO_2 industry is estimated to be $325.0 million in 2023 (IBISWorld 2023). The CO_2 is supplied to the food and beverage, construction and healthcare sectors, as well as other specialised users. The food and beverage sectors are the largest consumers of CO_2, as shown in Figure 14 below.

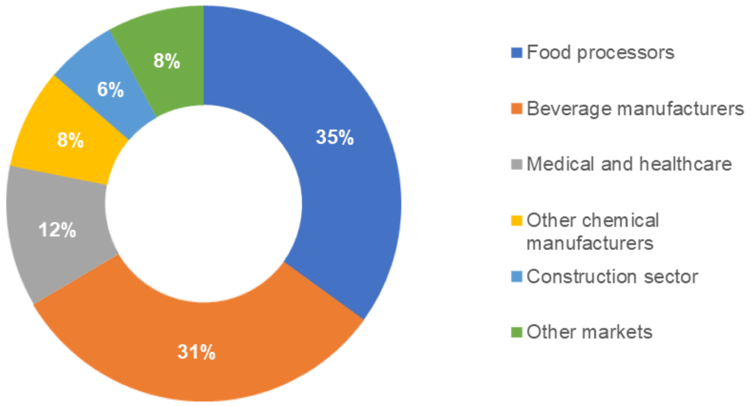

Figure 14: *Revenue segmentation of the Australian CO_2 industry in 2023 (IBISWorld 2023)*

Australian companies manufacture CO_2 in compressed, liquid and solid form. The CO_2 is purified to three main specifications, each with its own price point, i.e., industrial-grade, food-grade and laser-grade (IBISWorld 2023). This makes it difficult to estimate the quantities of CO_2 produced from revenue data alone.

Four companies account for the majority of CO_2 supply in Australia: Air Liquide Australia, BOC, Supagas, Wesfarmers; with market share as shown in Figure 15 below.

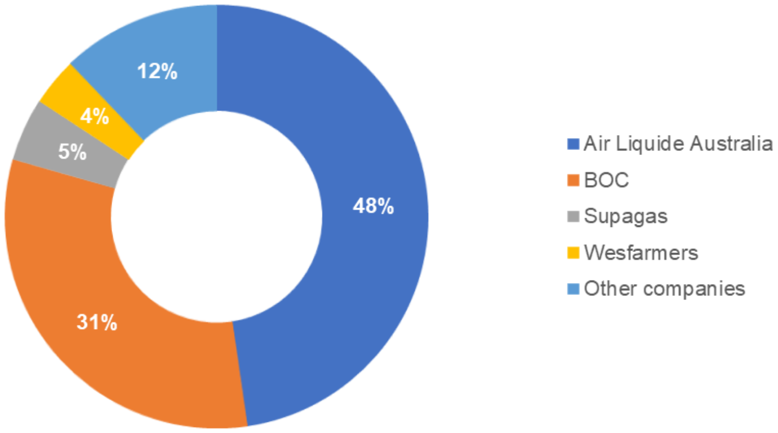

Figure 15: *Share of Australian CO_2 market by company (IBISWorld 2023)*

Of the CO_2 manufacturing facilities in Australia, 50.0% are located in Victoria, 33.3% in NSW, and 16.7% in WA. The CO_2 is usually a by-product that is purchased from industrial sources, including chemical plants and refineries. In Australia, a sizeable proportion of CO_2 is derived from ammonia produced to manufacture fertilisers and explosives (IBISWorld 2023).

Currently, Air Liquide Australia is constructing a new CO_2 processing and purification facility in collaboration with the Gippsland Basin Joint Venture (a 50:50 partnership between Esso Australia Pty Ltd and BHP Billiton Petroleum (Bass Strait) Pty Ltd). Esso's gas conditioning plant at Longford will be modified to allow capture of CO_2 from Gippsland natural gas processing, and the CO_2 will be sent to Air Liquide's new processing facility for purification. The CO_2 will be purified to food and beverage quality for use by Australian businesses.[21]

Thus, Victoria is currently the largest source of CO_2 in Australia, and Air Liquide Australia's new processing facility at Longford will ensure that this situation continues for the foreseeable future.

5.1.2 Potential New Sources of CO_2 in Victoria

5.1.2.1 Fossil fuel-derived CO_2

Until now, the CO_2 extracted during natural gas processing in Gippsland has been vented to the atmosphere. Air Liquide's new processing facility at Longford will allow a portion of this to become available for commercial use.

As Esso's oil and gas fields in Bass Strait reach the end of their working lives, they can be converted to CO_2 storage reservoirs, with potential capacity of 50-300 billion tonnes. Esso Australia recently announced the South Eastern Australia CCS Hub, which from 2024 will use existing gas extraction infrastructure to store CO_2 in the depleted Bream reservoir, located 46 km offshore in Bass Strait. Esso plans to store 0.5 Mt/y CO_2 in the Bream reservoir, and will make up to 1.5 Mt/y storage capacity available to third party users.[22] This means that, from 2024, a new CO_2 storage industry will be established in Gippsland. Large new quantities of CO_2 will then potentially become available for other purposes.

The proposed Hydrogen Energy Supply Chain (HESC) project, led by JPower and Sumitomo Corporation, will potentially be a participant in the new CCS Hub. From the late 2020s, the HESC project anticipates producing up to 225,000 t/y of ultrapure hydrogen for both local use and export to Japan, by gasification of Latrobe Valley lignite and CCS. At full capacity, the HESC project is anticipated to consume HESC project 4.74 Mt/y lignite and will capture 4.39 Mt/y CO_2 for storage (Kamiya et al. 2015).

The practical feasibility of all stages of the HESC concept have been successfully demonstrated. During 2020-2021, the HESC Pilot Project produced hydrogen at 99.999% purity by gasification of Victorian lignite and lignite-biomass blends in the Latrobe Valley. The gaseous hydrogen was transported by road to the Port of Hastings, where it was liquefied and loaded onto the *Suiso Frontier*,

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[21] https://www.exxonmobil.com.au/news/newsroom/news-releases-and-alerts/2022/construction-commences-of-processing-facility-to-recycle-co2

[22] https://www.exxonmobil.com.au/energy-and-environment/energy-resources/upstream-operations/the-south-east-australia-carbon-capture-hub

the world's first ocean-going liquid hydrogen carrier ship. The *Suiso Frontier* arrived at the Port of Kobe on 25 February 2022 and safely unloaded the hydrogen at a purpose-built receiving terminal and storage facility.[23]

Additional CO_2 storage capacity will be required to accommodate the large volumes of CO_2 generated by the HESC project and other large emitters in the state. The CarbonNet project, a joint initiative by the Victorian and Australian Governments, has established the feasibility of storing large volumes of captured CO_2 in the near-offshore region of the Gippsland Basin. The Pelican site, located approximately 8km off the Gippsland coast and 1.5 km beneath the seabed, has a proven CO_2 storage capacity of at least 125 million tonnes and a potential injection rate of 6 Mt/y.[24] Transportation of CO_2 by pipeline from the Latrobe Valley to sites in Bass Strait is one of the lowest-cost options for CO_2 sequestration in Australia, because of the short transport distance and the high permeability of the storage formations (CO2CRC 2015).

An independent assessment of the HESC project concept has demonstrated the feasibility of producing blue hydrogen and/or blue ammonia from Victorian lignite in a manner consistent with 'net zero by 2050' policy settings, largely due to the uniquely low fugitive methane emissions associated with Victorian lignite mining. Technology options exist to achieve a CO_2 capture rate in excess of 99% and by, co-gasification with a low percentage of biomass (2-5%), the process would achieve net-negative emissions (Kibria et al. 2023a; 2023b).

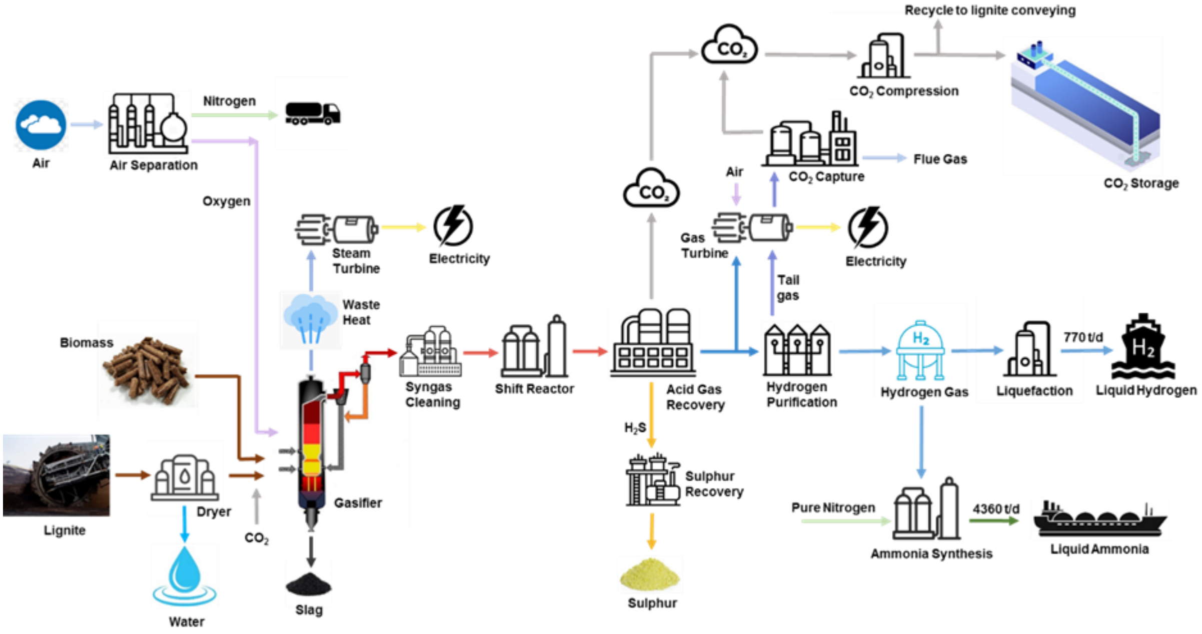

Figure 16: *Conceptual scheme for production of blue hydrogen and/or ammonia from Victorian lignite (Kibria et al. 2023b)*

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[23] https://www.hydrogenenergysupplychain.com/report-successful-completion-of-the-hesc-pilot-project

[24] https://earthresources.vic.gov.au/projects/carbonnet-project

The Committee for Gippsland has highlighted the unique competitive advantages of the region, with lignite, CO_2 storage capacity, wind and solar energy all available within a small geographical area. It recommends that blue hydrogen and CCUS should be commercialised as soon as possible, as the core of a chemical industry which produces ammonia, urea, and other value-added products. It recommends that *demand for clean hydrogen and derivatives must be stimulated to support investments in supply*, and that preparations should also begin to take advantage of the longer-term potential to produce commercial quantities of green hydrogen in Gippsland (Committee for Gippsland 2023).

5.1.2.2 Biogas-derived CO_2

A potential biogenic source of CO_2 in Victoria is as a by-product of biogas production. Biogas is produced by anaerobic fermentation of biological wastes, such as animal manure, crop residues and food waste. Biogas typically contains 53.0-57.7 vol.% CH_4, with the balance almost all CO_2, and has an energy content of 18,179-19,791 kJ m^{-3} (Walsh et al 1989).

Biogas can be combusted to produce electricity, and is considered a form of renewable energy. In 2023, the Victorian Government made more than $8 million available through the Waste to Energy – Bioenergy Fund for 24 new projects that are forecast to boost Victoria's renewable energy capacity by an additional 6.82 MW.[25]

In a study conducted for Sustainability Victoria, Enea Consulting estimated Victoria's recoverable biogas potential to be between 10.5 PJ and 24.9 PJ per year[26] (Enea Consulting 2021). This is the equivalent of 553.1 – 1311.6 x 10^6 m^3/y biogas.[27] If all this biogas was used to produce electricity, the total amount of CO_2 emitted would be in the order of 1.0 – 2.4 million t/y CO_2.

Most of the potentially recoverable biogas in Victoria is based on agricultural cropping residues, which have the disadvantage of being seasonal and widely dispersed, not to mention being essential for maintaining the carbon content of the soil. The most concentrated sources of biogas in Victoria are in the Melbourne metropolitan region, associated with food organics in the wastewater treatment systems (Enea Consulting 2021).

For example, Melbourne Water's Western Treatment Plant in Werribee (see Figure 17 below) uses floating lagoon covers to collects over 60,000 m^3 of biogas per day from its primary treatment lagoons for renewable energy conversion, generating over 40% of the site's electricity requirements.[28] The emissions from this quantity of biomass equate to about 40,000 t/y CO_2.

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[25] https://www.premier.vic.gov.au/transforming-todays-waste-tomorrows-energy

[26] 1 PJ = 10^{12} kJ

[27] At an average energy content of 18,985 kJ m^{-3}

[28] https://www.evoqua.com/en/case-studies/melbournewater-municipal-biogas-cover/

Figure 17: *Melbourne Water's Western Treatment Plant in Werribee* [29]

The Western Treatment Plant treats around 50% of Melbourne's sewage, while the Eastern Treatment Plant treats 40%. Thus, the total amount of CO_2 potentially recoverable from the metropolitan water treatment system is about 80,000 t/y.

In addition, Yarra Valley Water operates a waste-to-energy plant, known as ReWaste, next to its existing Aurora sewage treatment plant in Wollert (see Figure 18 below). The facility handles an annual volume of 33,000 tonnes of commercial and industrial biowaste (Enea Consulting 2019), and is estimated to generate about 20,000 t/y CO_2.

Figure 18: *Yarra Valley Water's ReWaste Facility (© Weltec Bio Power GMBH)*

Thus, three water treatments plants in the Melbourne metropolitan area collectively produce about 100,000 t/y CO_2 which, if captured and stored, would qualify as carbon-negative emissions. Recognising this opportunity, technology developers now offer modular CO_2 capture systems suited to

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[29] https://www.evoqua.com/en/case-studies/melbournewater-municipal-biogas-cover/

this scale of operation, that can be delivered prefabricated for easy installation. Carbon Clean[30], Aker Carbon Capture[31], and Mitsubishi Heavy Industries[32] each offer systems suited for capturing CO_2 emissions from wastewater treatment plants, as shown in Figure 19 below.

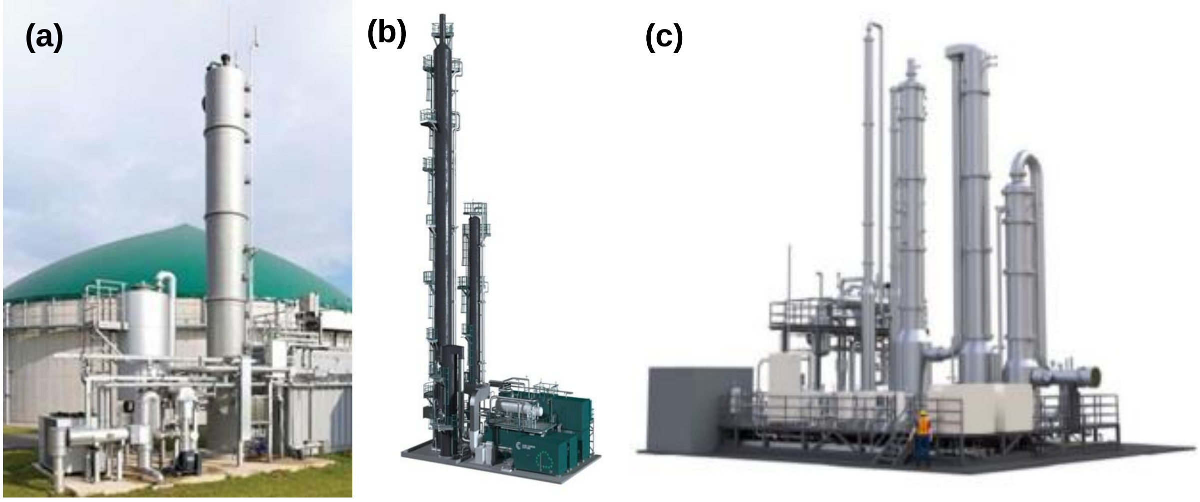

Figure 19: *Modular CO_2 capture systems from (a) Carbon Clean, (b) Aker Carbon Capture, and (c) MHI*

While the quantity of biogenic CO_2 available in Victoria are very small in comparison to the fossil-derived CO_2 available in the state, it is a valuable resource because it is carbon-neutral and carbon-negative if permanently sequestered, e.g., in concrete. This offers both a potentially valuable market advantage for local businesses, as well as an additional contribution to meeting the State's emissions abatement targets.

5.2 POTENTIAL NEW APPLICATIONS FOR CO_2

There are three applications for the direct use of CO_2 which provide potential opportunities for CO_2 recycle in the Latrobe Valley - supercritical CO_2 extraction, electricity generation via the Allam Cycle and enhanced oil recovery. Each of these are discussed in the sections below.

5.2.1 Supercritical CO_2 Extraction

5.2.1.1 Background on Supercritical CO_2 Extraction

Supercritical carbon dioxide (S-CO_2) is an attractive alternative in place of traditional organic solvents. Unlike many organic solvents, S-CO_2 is non-flammable. It is inert, non-toxic and has a relatively low cost. Its solvation strength can be fine-tuned by adjusting the density of the fluid. CO_2 leaves a lower amount of residue in products compared to conventional solvents, and it is available in relatively pure

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[30] https://www.carbonclean.com/modular-carbon-capture-systems
[31] https://akercarboncapture.com
[32] https://www.mhi.com/products/engineering/co2plants_process.html

form and in large quantities. Dissolved compounds can be recovered from S-CO_2 simply by reducing the pressure and/or increasing the temperature, leaving the recovered product free of residual solvent. S-CO_2 extraction is regarded as producing high-grade extracts and is accepted for manufacture of organic food products.

5.2.1.2 The process of supercritical CO_2 extraction

S-CO_2 extraction makes use of the unique properties of carbon dioxide when it is compressed to a temperature and pressure when it becomes ‘supercritical’. In the supercritical state, i.e. above its critical point temperature and pressure (32.1 ^oC, 73.8 bar), CO_2 has a liquid-like density, it exhibits gas-like diffusivity, surface tension and viscosity. Its gas-like viscosity results in high mass transfer. Its low surface tension and viscosity lead to greater penetration into porous solids. Because of its liquid-like density, its solvent strength is comparable to that of a liquid.[33]

Under supercritical conditions, CO_2 becomes a tuneable solvent. Its fluid density and density-dependent properties are very sensitive to pressure and temperature changes. The solvent power of a supercritical fluid is approximately proportional to its density. Thus, solvent power can be modified by varying the temperature and pressure.

The principle of S-CO_2 extraction is illustrated in Figure 20 below. The feed material is typically ground solid material, which is fed to the extractor. Most commercial operations for supercritical fluid extraction are batch or semi-batch operation especially when the feed material is solid. For liquid feed material, the extraction occurs in a countercurrent column filled with random or structured packing material. However, for highly viscous liquid feed, the viscous liquid and supercritical fluid may be mixed and sprayed through a nozzle into the extractor vessel.

S-CO_2 extraction is a high pressure process, and all equipment must be built and certified to suit. As the scale of the process and the volume to be extracted increase, the vessel walls become very thick. Food-grade stainless steel is usually the material of choice, so large scale S-CO_2 is a significant capital investment.

The raw materials are extracted by recirculating S-CO_2 for 4-6 hours. During this time, the concentration of extracted material gradually increases in the recirculating CO_2. When the extraction is complete, the product is recovered by depressurising the system in a controlled manner, which reduces the solubility of the product. Separate separation stages may be used, allowing the product to be fractionated based on solubility in CO_2 at different pressures.

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[33] www.chemengonline.com/supercritical-co2-a-green-solvent/?printmode=1

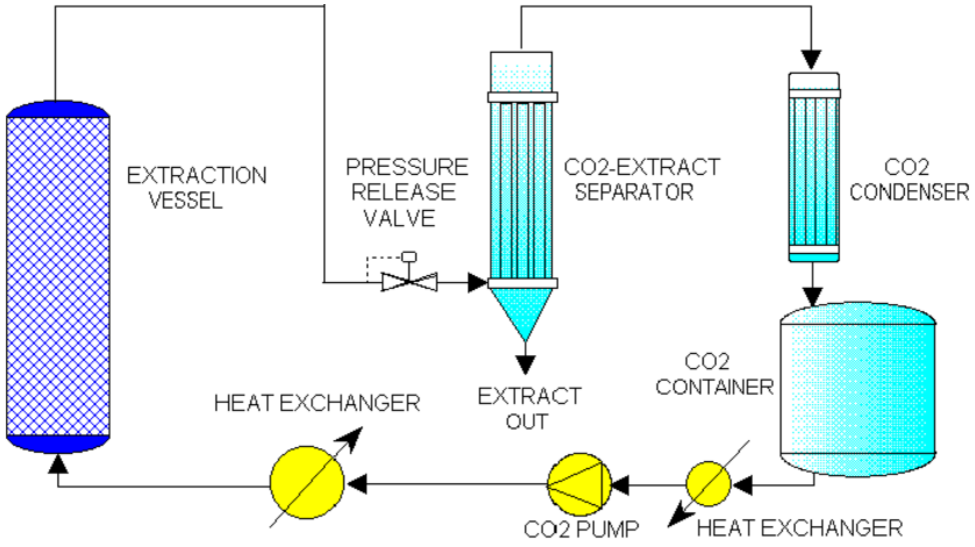

Figure 20: *The supercritical CO_2 extraction process (Laitinen 1999)*

One of the issues to be aware of with S-CO_2 is that during extraction, the extracted material recirculates continuously with the CO_2 throughout the entire plant. Typically, this means that at the end of each batch, the entire system must be stripped down and cleaned very thoroughly to prevent cross-contamination between batches. This adds to the cost of production of each batch.

A S-CO_2 facility can essentially be run in one of three modes of operation.

1. Producing a single high volume, moderate value product for most of the time, to maximise the capacity of the plant and minimise downtime.
2. Producing multiple low volume, high value products such as nutraceuticals, in a food-grade facility under good manufacturing practice (GMP) conditions.
3. Producing multiple low volume, high value products such as pharmaceuticals, in a TGA-approved GMP facility.

Most S-CO_2 facilities fall into the second category, as the cost of constructing and operating a pharmaceutical-grade facility is prohibitive. In practice, pharmaceutical products would be manufactured by upgrading nutraceutical-grade material in a separate facility.

5.2.1.3 Applications of supercritical CO_2 extraction

Currently, the widest application of S-CO_2 is in extraction. Decaffeination of coffee was one of the first processes commercialised using S-CO_2. Extraction of hops during the beer brewing process is another area where CO_2 is used. There are many applications for S-CO_2 extraction in the preparation of high value products, such as flavours, colours and fragrances, food supplements and nutraceuticals.

Extraction of food and natural products using S-CO_2 can be considered a relatively mature technology. A wide range of other applications for S-CO_2 has been investigated, including chemical reactions, polymer production and processing, semiconductor processing, powder production, environmental and soil remediation and dry cleaning. Supercritical CO_2 extraction can also be used to purify materials that are used for the production of medical devices.

One of the promising new applications for S-CO_2 extraction is in vegetable oil production. The conventional process is based on solvent extraction using hexane, which is regarded as a hazardous air pollutant. S-CO_2 extraction is gaining in popularity as a clean alternative, as it produces a high-quality product and de-fatted meal free of residual solvent (Dhara et al. 2022). Large-scale S-CO_2 extraction is currently limited to semi-continuous batch operation, but it is employed at industrial scale for upgrading of soy flakes and cocoa nibs, with recovery of the seed oil as a by-product (Ahangari et al. 2021). Tandem processing employing conventional expeller pressing followed by SC-CO_2 treatment of the residual meal to further enhance the oil recovery is currently practiced on substrates such as hemp seeds, sesame meal and rice bran. The combination of expelling and S-SCO_2 extraction results in high yields and superior quality oils (Bañares et al. 2023).

New products are being created from seeds that are normally discarded as food-processing waste, such as grape seed, raspberry seed and date seed. However, the greatest focus in recent years has been on industrial production of hemp (*Cannabis sativa* L.) seed oil (Ahangari et al. 2021). Hemp seeds contain 25‑35% oil and are a rich source of polyunsaturated fatty acids (> 70%), particularly the essential fatty acids linoleic acid and α-linolenic acid. Hemp oil extracted using S-CO_2 has higher antioxidant content and less pigment than cold pressed oil (Burton et al 2022). Hemp seeds also contain 20‑25% protein, containing all the essential amino acids needed for human health. Hemp seed flour has superior nutritional quality compared to wheat flour and is approved for use in food products (Burton et al 2022).

5.2.1.4 Supercritical CO_2 drying

Drying of food products is a specific application of S-CO_2 extraction, in which the material to be extracted is water. The S-CO_2 drying process works in a similar way to air drying, except that the drying medium consists of CO_2 under pressure. Under supercritical conditions, the CO_2 can easily permeate and readily evaporate the water from food products. This results in faster drying times and reduced energy consumption. Products dried using S-CO_2 keep their colour and shape, so they look natural and fresh. As the drying process is done at relatively low temperatures in an oxygen-free environment, the vitamins, pigments and proteins are preserved, ensuring that the nutritional value is retained. At the same time, S-CO_2 also inactivates microorganisms that can lead to spoilage, thus avoiding the need for further pasteurisation. S-CO_2 drying has been shown to be effective for a range of fruits, vegetables and herbs, including berries, apples, mangoes, broccoli, carrots, and basil.[34]

Commercial S-CO_2 drying of food is promoted by CO2Dry (part of the FeyeCon Group) in the Netherlands, which has a patent on the technology (Agterof et al. 2005). It has established a 500 litre pilot scale S-CO_2 drying unit,[35] which it uses for toll manufacturing and business development.

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[34] https://www.tasteofscience.com/articles/1275/drying-with-supercritical-co2.html

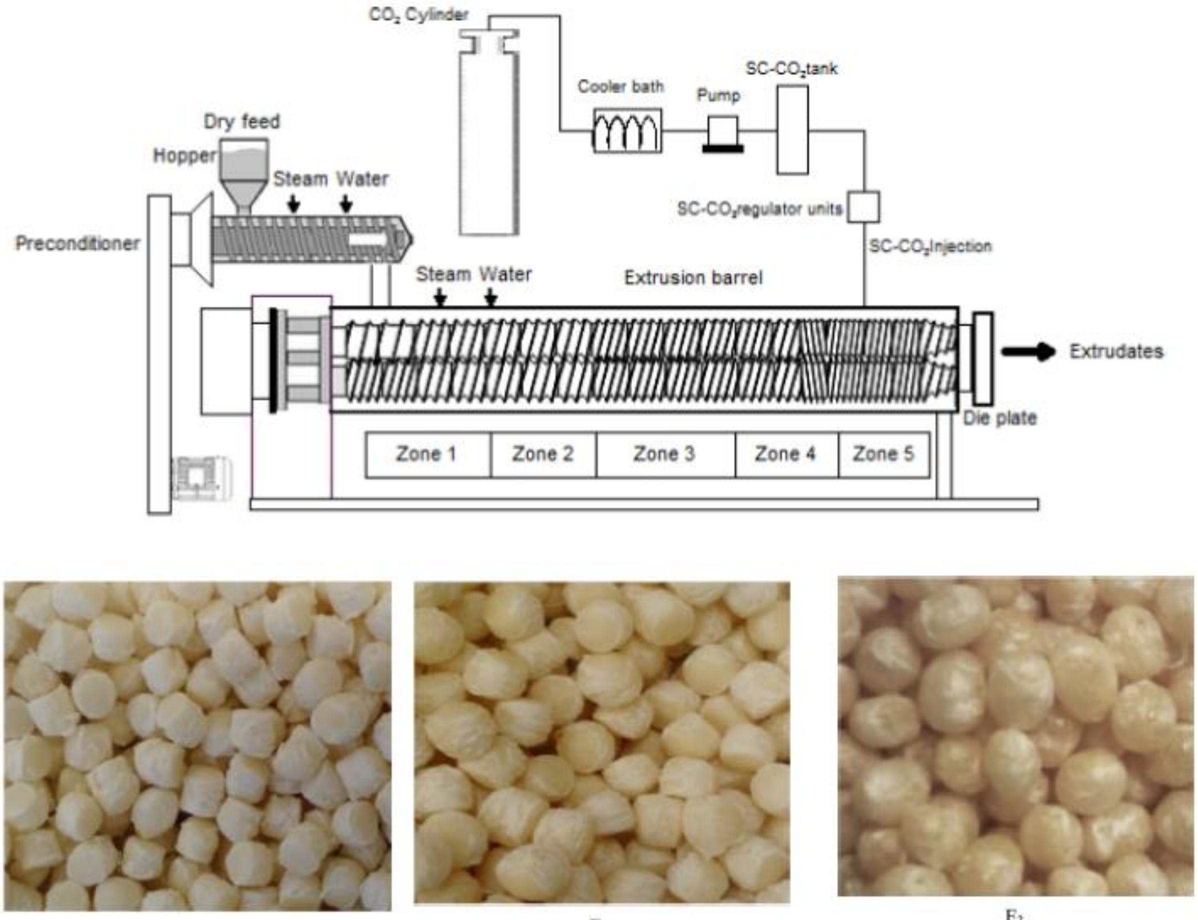
[35] http://www.future-food.eu/

Figure 21: *S-CO_2-dried food ingredients: raspberry, algae, egg-white powders © CO2Dry*

5.2.1.5 Supercritical CO_2 extrusion

Extrusion is one of the most important food processing innovations of the 20th century, and is widely used in manufacturing a diverse range of food products including pasta, snacks, breakfast cereals, confectionary, texturised meat substitutes, infant food formulations, precooked beverage powders and extruded crispbread. Traditional extrusion uses steam expansion as the driver for expanding or 'puffing' the extruded product (Panak-Balentić et al. 2017). This involves relatively intense processing conditions such as high temperatures, high shear and low moisture, particularly when higher expansion is required. The extreme extrusion operating conditions are often very destructive to heat-sensitive ingredients such as proteins, vitamins and other bioactives (Zhou et al. 2021).

Supercritical fluid extrusion (SCFX) is a novel process combining extrusion and supercritical fluid technologies to utilise supercritical CO_2 as the blowing agent for puffed products instead of steam. Without needing steam, SCFX can operate at lower temperatures (below 100 °C) and at lower shear rates, allowing heat-sensitive food ingredients to be included in extrudate formulations (Zhou et al. 2021). A typical SCFX system and some puffed products based on milk protein are shown in Figure 22 below.



F$_1$ F$_2$ F$_3$

Figure 22: *SCFX system and photographs of milk protein-based extrudates (Zhou et al. 2021)*

Supercritical CO_2 extrusion enables the production of a wide range of food products, including breakfast cereals, snack foods, pasta, chocolate and confectionery, as well as unleavened conventional and gluten-free bread. These products have improved properties and better nutritional quality than with conventional extrusion, and require less energy to manufacture. This represents an opportunity for development of innovative and nutritious convenience foods (Panak-Balentić et al. 2017).

5.2.1.6 Supercritical CO_2 dyeing

DyeCoo, based in Hoofddorp, the Netherlands, has developed the world's first 100% water-free and process chemical-free textile processing system, using S-CO_2 technology. Conventional textile dyeing requires large amounts of water and produces wastewater filled with dye and chemicals. DyeCoo found that textile dyes are readily solubilised in S-CO_2, so the dyes need no chemical processing and can penetrate fabrics easily. The process uses no chemicals or water, produces no wastewater, requires no drying time because the dried fabric comes out dry, and 95% of the CO_2 is captured and reused in a closed loop system. Because the dye is used so efficiently and there is no wastewater treatment needed, costs are reduced by 40-60%. Moreover, the process can be employed anywhere, since it doesn't require water. DyeCoo technology is currently being used in Nike, Ikea, Adidas and Peak Performance products and in commercial mills in Thailand and Taiwan.[36]

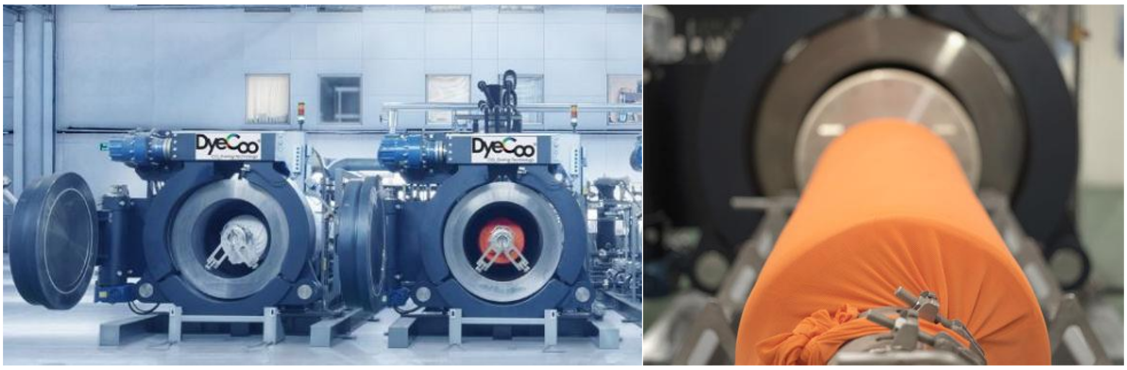


Figure 23: *DyeCoo supercritical CO_2 textile dying system* [37]

5.2.1.7 Victorian Research Context

Pharmalink Extracts Limited, in Nelson, New Zealand operates a modern, high quality S-CO_2 plant suitable for food-grade and nutraceutical-grade manufacture. S-CO_2 extraction is accomplished using 3 x 850 litre extraction vessels with two separation stages for product fractionation, built by NatEx of Austria. There is also a 6 litre capacity pilot-scale S-CO_2 system, which is useful for developing the optimal set of conditions for extraction at production scale. The mainstay of the Pharmalink Extracts business is hops extraction for the brewing industry. It also produces high-value products in the nutraceutical, functional food and health ingredient markets.

In Australia, the only production scale S-CO_2 facility is operated by Essential Oils of Tasmania, at Kingston, which is used to extract fragrances for perfume manufacture.[38] The extraction capacity of this facility is not known.

Given that a medicinal cannabis industry is being developed in Victoria, and the global interest in developing pharmaceutical products from cannabinoid fractions, it seems inevitable that small-scale S-CO_2 extraction will eventually be deployed for this purpose. Currently, the only research in Australia to support this application is being conducted at the University of Queensland (Qamar et al. 2021).

5.2.1.8 ACI Comments

Supercritical CO_2 extraction is a well-established technology that is used at large scale for extraction of coffee, oil seeds and hops. It has a TRL of 9 for extraction of solid materials. Extracts produced using S-CO_2 are currently sold in Australia, predominantly produced in China. Supercritical CO_2

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[36] https://dyecoo.com/

[37] https://www.textiletechnology.net/technology/news/tau-investments-in-eco-friendly-textile-dyeing-technology-32784; https://www.ecotextile.com/2013120312334/dyes-chemicals-news/nike-sees-co2-dyeing-as-revolutionary.html

[38] https://www.themercury.com.au/lifestyle/tasmanian-farmers-on-the-scent-of-lucrative-new-market/news-story/bb71da63cbd5be9ce6452c7c4f9c0743

extraction is a high value, low volume process that could readily be established in Victoria to produce a range of specialist products for the food, nutraceuticals and cosmetics markets. Globally, the vegetable extracts market was valued at over US$31.8 million in 2021 and is estimated to expand at 6.7% p.a., reaching US$60.9 million by the end of 2031.[39]

Victoria has one local textile dyeing company, Geelong Dyeing, which has been operating for over 40 years and offers bespoke dyeing and finishing services for clients ranging from individuals to commercial operations, fashion apparel, uniforms, upholstery and soft furnishings.[40] *It is well positioned to take advantage of the DyeCoo process, which would be a first for Australia.*

Victoria is rich in agricultural resources, which can potentially be upgraded to high value products with the aid of supercritical CO_2 *extraction, drying or extrusion. S-*CO_2 *processing offers opportunities for producing new types of products from by-product streams that would otherwise go to waste. For example, the Latrobe region produces a wide range of vegetables such as leafy vegetables, potatoes, beans, sweet corn, broccoli, asparagus, snow peas and tomatoes. Inevitably, production of such products involves a degree of wastage, with off-specification product usually being disposed of as stock feed. S-*CO_2 *processing can potentially be used to produce high value food additives from such materials, such as natural colours, and antioxidant-rich powders. For example, the red pigment lycopene can be extracted from tomato waste (Kehili et al. 2017) and antioxidant phenolic compounds from asparagus (Solana et al. 2015). Similarly, the Latrobe region is home to a number of flower farms. S-*CO_2 *extraction can be used to extract essential oils and aromas from flowers. For example, lavender essential oil is commercially produced using S-*CO_2 *extraction (Danh et al. 2012).*

One of the most prospective opportunities in Victoria would seem to be in relation to industrial hemp cultivation. Hemp can be grown to produce hemp seed for food purposes. Hemp also has potential applications in a diverse range of products including industrial purposes (textiles, biocomposites, paper, automotive, construction, biofuel), functional foods, oils, cosmetics, personal care, and pharmaceuticals, as shown in Figure 24 below.

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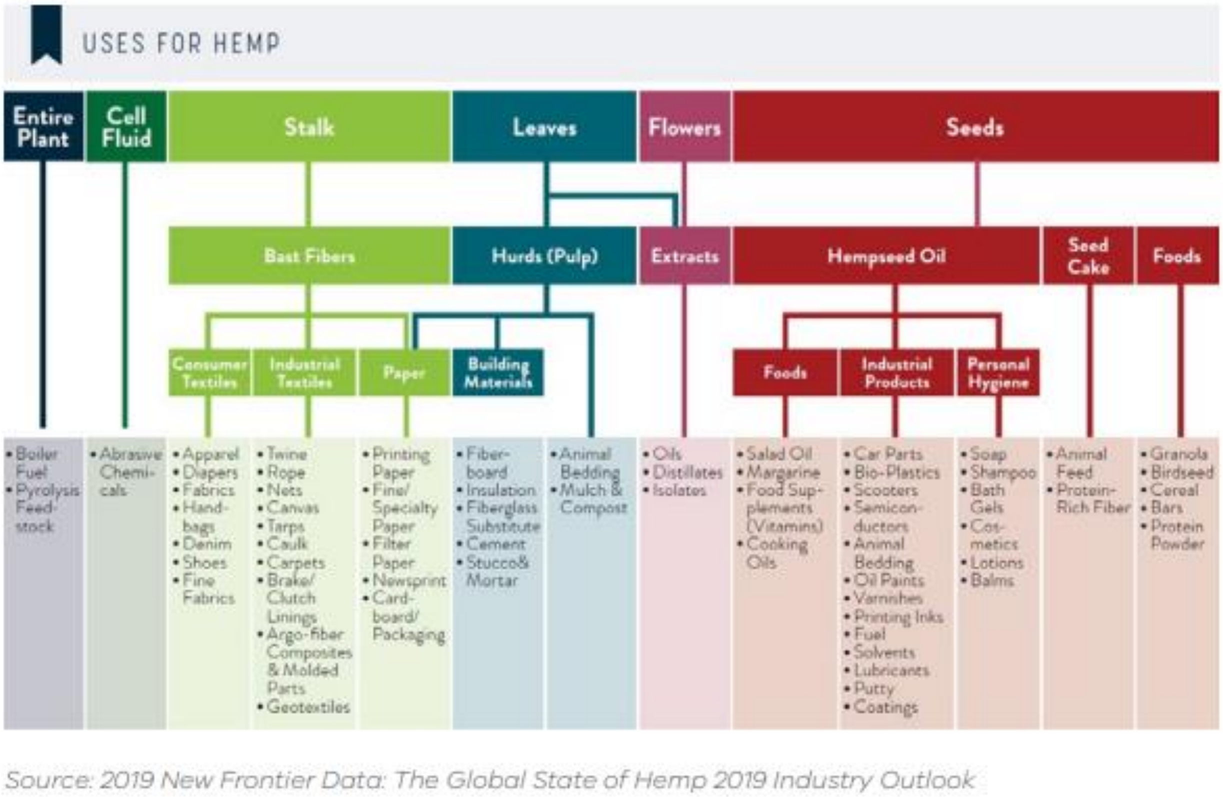
[39] https://www.transparencymarketresearch.com/vegetable-extracts-market.html
[40] https://www.geelongdyeing.com.au/



Source: 2019 New Frontier Data: The Global State of Hemp 2019 Industry Outlook

Figure 24: *List of potential industrial hemp products (State of Victoria 2020).*

Industrial hemp is a high yielding, hardy and fast-growing annual crop. Commercial or trial hemp crops are grown in all states in Australia. Most Australian commercial production is in Tasmania. In the 2019-20 growing season, approximately 1600 hectares was planted in Tasmania, with a farm gate value of $4.5 million. In Victoria, hemp is mainly grown to produce seed for food purposes. Approximately 200 hectares of hemp was planted in the 2019-20 growing season, down from 600 hectares in 2017-18 due to low water availability (State of Victoria 2020).

Victoria is well placed to capitalise on the growing market for industrial hemp products, with a global market currently worth about $7 billion a year and expected to grow to more than $27 billion by 2027. The most straightforward application of hemp is for fibre as a construction material. A crop of industrial hemp can be grown in 100 days, with five thousand hectares potentially contributing $100 million into the local economy.[41] *Local hemp-based construction companies, such as ProHemp in Pakenham, The Hemp Building Company in Kyneton, and Hempcrete Australia in the Mornington Peninsula, are well placed to capitalise on this opportunity.*

Industrial hemp is also a prospective feedstock for renewable bioenergy production, yielding 100 GJ/ha/y (Parvez et al. 2021). It could potentially be developed for blue hydrogen production via

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[41] https://www.abc.net.au/news/2023-06-01/industrial-hemp-vying-for-victoria-government-boost/102415910

gasification with CCS, as proposed by the Hydrogen Energy Supply Chain consortium, where it could help to reduce CO_2 emissions to net zero.

The market for hemp seeds as a food source is expected to grow significantly, as hemp seed protein contains all the essential amino acids need for human health (Burton et al. 2022). New food applications are being developed for hemp seed flour, including plant-based milk alternatives (Nissen et al. 2020), meat analogues (Zahari et al. 2020), and as a substitute for wheat flour in bread (Rusu et al. 2021).

Hemp seed oil has a good taste and various advantages over other vegetable oils (e.g., soybean oil, canola oil, and palm oil) with high levels of fat-soluble provitamin A, vitamin E, and minerals. It contains more than 80% polyunsaturated fatty acids, and is rich in both ω-6 and ω-3 essential fatty acids, with an optimal ratio for human metabolism. Expeller pressing of hemp seeds yields 23% oil, with 10% oil in the residual residue in oil cake, which can be reduced to only 0.4% using S-CO_2 extraction (Xu et al. 2021). Hemp seed oil is well placed to take an increasing share of the global vegetable oil market, which was valued at US$2.52 billion in 2021, and is expected to grow to US$3.73 billion by 2028.[42]

An opportunity may exist for a specialised ingredient production business in the Latrobe Valley, drawing upon the agricultural products produced in the region as well as specialised products such as Australian native foods. It is likely that a single supercritical CO_2 facility in the region could service a number of different business clients, and would benefit from a close association with Federation University in Churchill. ***ACI recommends that a separate study be undertaken to investigate the business case for such an enterprise.***

The Victorian Government is currently supporting development of a local medicinal cannabis industry. It is still early days but indications from the United States, where the market is more advanced, suggest that the development of tailored cannabis products will progress from dried plant material and oil extracts to S-CO_2 extracts and more advanced delivery systems, e.g., patches, vapes, etc. At an appropriate time, specialist expertise gained through a local hemp seed processing industry could easily be leveraged to create higher-value market opportunities in the pharmaceuticals sector. The CO_2 is recovered and recycled.

5.2.2 CO_2 as a Working Fluid for Heat Recovery via the Allam Cycle

5.2.2.1 Current Status

To meet the need for secure, reliable, clean and sustainable energy, a broad portfolio of energy conversion and storage technologies will be required, including blue and green hydrogen, concentrated-solar power, fossil fuels and biomass with CCS, direct air capture, ammonia, methanol, etc. Despite the diversity of these technologies, one thing that they all have in common is that they produce waste heat, representing a loss of energy efficiency and a potential disposal/treatment cost.

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[42] https://www.vantagemarketresearch.com/

Hence there has been a surge in research efforts over the past decade to develop efficient ways to recover waste heat to complement the growth of clean energy technologies.

The thermodynamic power cycles that are employed in boilers and internal combustion engines, typically involve the Rankine cycle and the Joule–Brayton cycle, which operate with water or air respectively. These are most efficient at high temperatures and are not favourable for recovery of lower-grade heat. Consequently, supercritical carbon dioxide (S-CO_2) power cycles are emerging as a promising alternative, with the advantage of having high thermal efficiencies with heat sources in the range of 300 – 800 ^oC (White et al. 2021). S-CO_2 has higher density and incompressibility than steam or air, leading to the following benefits (Macadam et al. 2019):

- Higher cycle efficiencies due to the unique fluid and thermodynamic properties of S-CO_2
- Reduced emissions resulting from lower fuel usage
- Compact turbomachinery, resulting in lower cost, reduced plant size and footprint, and more rapid response to load transients
- Reduced water usage, including water-free capability in dry-cooling applications
- Heat source flexibility

As a result, supercritical CO_2 technology offers a broad potential for power generation and propulsion, as summarised in Figure 25 below.

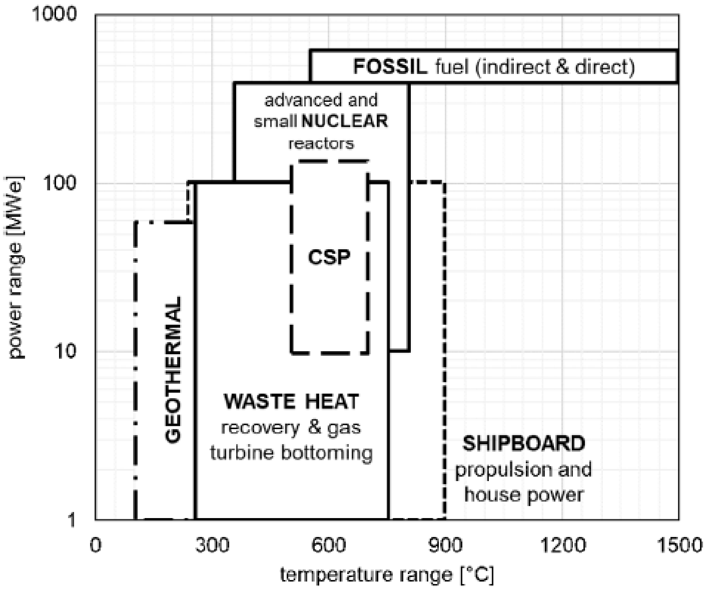

Figure 25: *Overview of sCO_2 power applications (White et al. 2021)*

In the renewable energy sector, S-CO_2 systems are being investigated for concentrated solar power (CSP), geothermal energy (White et al. 2021), and heat recovery from electrolysis systems (Shasmi et al. 2023). In the fossil fuel sector, S-CO_2 systems are well established and commercial solutions are available for gas turbines, reciprocating internal combustion engines, waste heat recovery, the bottoming cycle of steam boilers, and energy intensive industries (White et al. 2021).

A significant recent development in this field was the invention of the Allam cycle (Allam et al. 2013). In the Allam Cycle, shown in Figure 26 below, the fuel is combusted in a mixture of oxygen and recirculated CO_2, with the resulting hot gas used to drive a turbine to generate electricity.

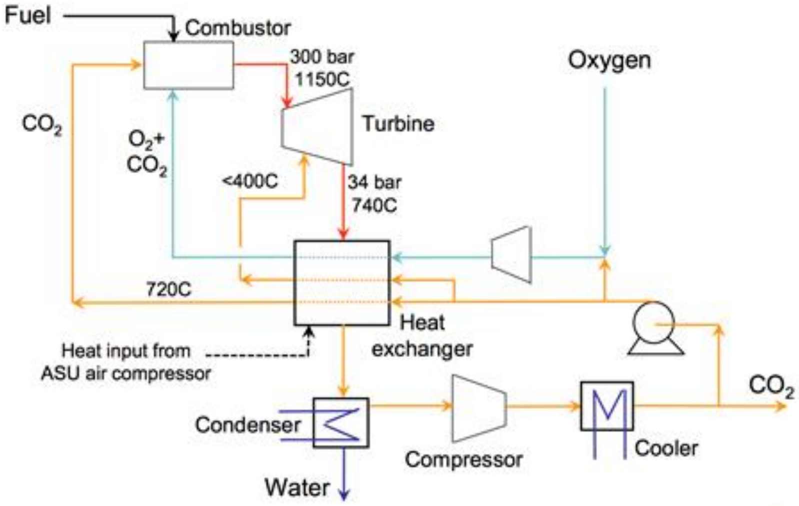

Figure 26: Natural gas Allam Cycle process outline[43]

The high temperature exhaust gas from the turbine is cooled in an economiser heat exchanger, with the heat being transferred to a high-pressure CO_2 recycle stream that flows into the combustor, diluting the combustion products and lowering the turbine inlet temperature to an acceptable level. The turbine exhaust flow is cooled to a temperature below 70°C in the economiser heat exchanger and then further cooled to near atmospheric temperature in an ambient air cooler or with cooling water.

Combustion of the fuel produces water vapour and additional CO_2. The water is removed in the condenser, and the remaining stream of predominantly CO_2 is compressed to the required high pressure. The recycle stream is then reheated in the economiser heat exchanger before returning to the combustor. The net CO_2 product derived from the combustion of fuel with pure oxygen in the combustor is removed from the high-pressure stream recycle at a high purity and pressure for delivery to an export CO_2 pipeline (Allam et al. 2017).

The advantage of the Allam Cycle is that it provides for close to (or at) pipeline grade CO_2 as part of the operating process. This dramatically increases the efficiency of producing CO_2-free electricity, as in a conventional power plant, the efficiency loss associated with CO_2 capture can be upwards of 25%.

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[43] Mancuso et al. 2015

The Allam Cycle is currently being commercialised by NET Power, a collaboration between Exelon Generation, McDermott, and 8 Rivers Capital. It has constructed a demonstration plant in La Porte, Texas, which includes a new 50MW combustor and turbine designed by Toshiba. In May 2018, NET Power announced that it had successfully achieved first firing of the plant, demonstrating the feasibility of operating the combustor with full CO_2 recycle.[44] In parallel with these demonstration plant tests, NET Power is advancing the development of commercial-scale 300MWe natural gas plants, including the development of a 300 MWe utility scale oxy-fuel sCO_2 turbine that will burn natural gas-fired, coal syngas and even hydrogen mixtures capable of 1,150°C turbine inlet temperature at 300 bar (Moore et al. 2023).

NET Power is also designing a solid fuel option for the Allam Cycle (Allam et al. 2017). The adaptation of the technology to solid fuel is apparently relatively straightforward and is compatible with conventional high temperature slagging, water quench gasifiers (see Figure 27 below), however NET Power have yet to demonstrate the integration of the technology in the solid fuel sector.

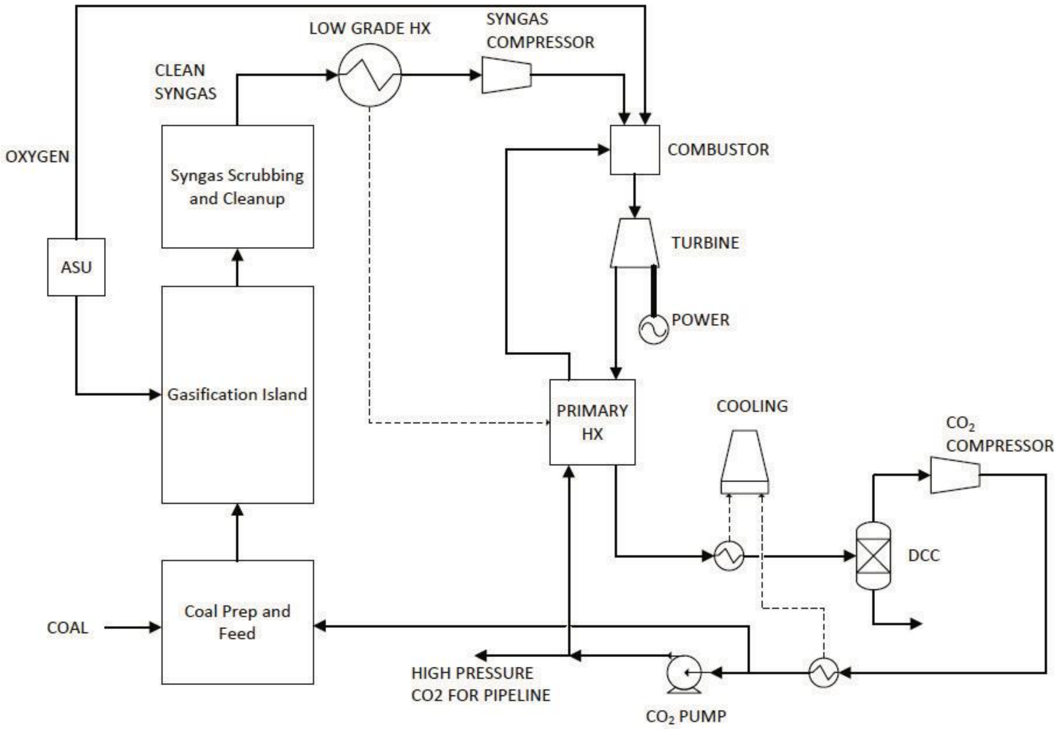

***Figure 27:** Process schematic of the solid fuel Allam Cycle*[45]

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[44] https://www.prnewswire.com/news-releases/net-power-achieves-major-milestone-for-carbon-capture-with-demonstration-plant-first-fire-300656175.html
[45] Lu et al. 2016

Various conceptual studies have demonstrated the feasibility of integrating the Allam cycle into both coal and biomass gasification (Fu et al. 2023), incorporating lignite drying (Lu et al. 2019), polygeneration of power with methanol (Xin et al. 2021) ammonia (Wang et al. 2021; Byun et al. 2022), and ethylene glycol (Zhou et al. 2023). These studies demonstrate the potential of the Allam cycle to effectively decarbonise the gasification process and support production of value-added, low-emissions products.

5.2.2.2 ACI Comments

The TRL of the Allam Cycle is effectively 8 with CH_4*, since the Toshiba 50MW combustor and turbine currently being demonstrated will be scaled up in parallel for commercial operation.*

This development suggests that there could be the potential to utilise the Allam Cycle technology in Victoria in the near future, particularly when considering the significant CO_2 *storage capacity available in the state. Gasification of lignite or biomass could be used to produce both electricity and a synthesis gas (syngas) suitable for conversion to products such as fertiliser and hydrogen.*

The ability to 'bolt on' the Allam Cycle to the existing electricity production process makes this technology one of the more promising ways to recycle CO_2 *from industrial processes, subject to the proof of operation with solid fuel.*

5.2.3 Enhanced Oil Recovery

5.2.3.1 Current Status

Enhanced oil recovery (EOR) is a term used for a variety of techniques for increasing the amount of crude oil that can be extracted from an oil field. EOR is used to extend the working life of oil fields and make them more profitable. There are three primary techniques of EOR: gas injection (CO_2, natural gas or nitrogen), thermal injection, and chemical injection. Gas injection using CO_2 (CO_2-EOR) is currently the most commonly used method.

CO_2-EOR was first deployed in the 1970's in the United States and is considered a commercially mature technology. Experience over the past 40 years has shown that virtually all of the CO_2 that is injected remains contained in the pore spaces of the oil reservoir (Office of Fossil Energy 2014). Consequently, CO_2-EOR is both a CO_2 utilisation process as well as a permanent CO_2 sequestration method.

Generally, EOR relies on the solvent properties of CO_2 to dissolve in and decrease the viscosity of the oil (miscible CO_2 flooding) as shown in Figure 9 below. However, immiscible CO_2 flooding may be utilised for heavy crude oil, with the mechanism for oil recovery more associated with gravity displacement. In each case, CO_2 is separated from the oil at the surface for re-injection.

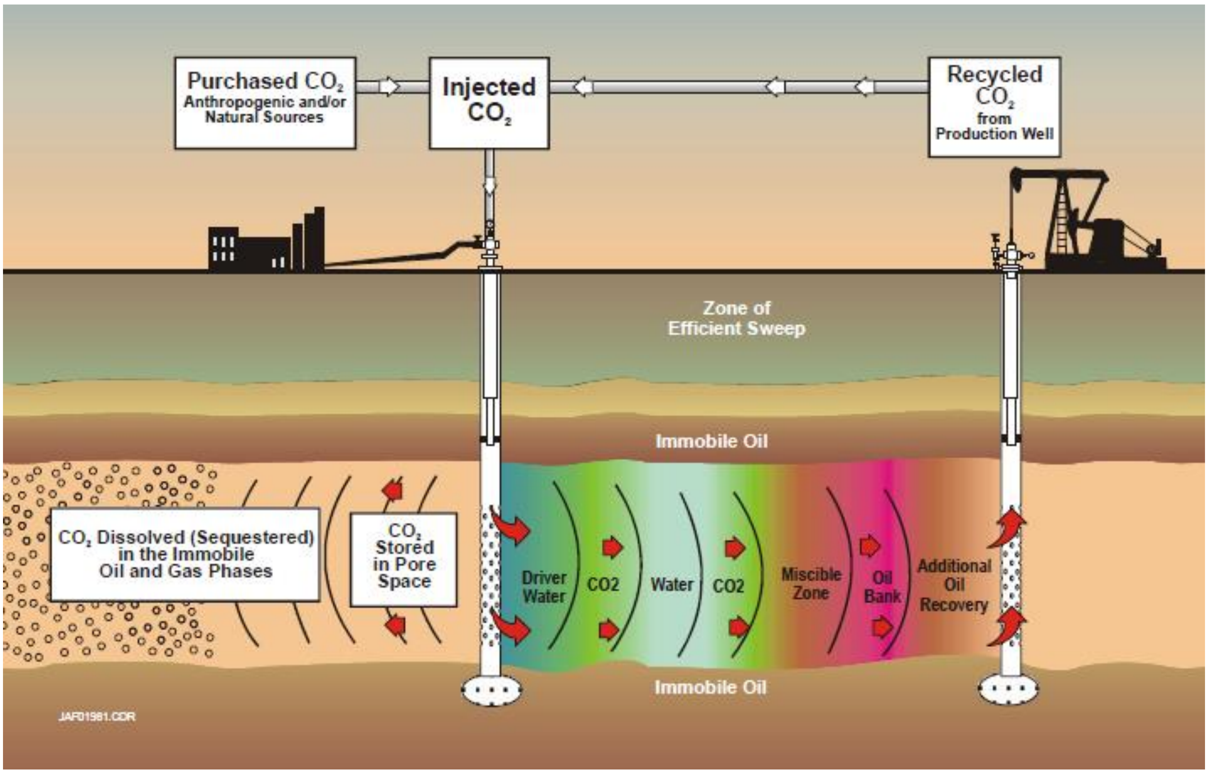

Figure 28: *Schematic showing the miscible CO_2-EOR process*[46]

The United States is by far the biggest user of CO_2-EOR. There are currently 114 active commercial CO_2 injection enhanced oil recovery (EOR) projects in the United States that collectively inject over 1.8 Mt y^{-1} CO_2 and produce over 280,000 barrels of oil per day (Saini 2017). Extensive EOR operations also exist in Canada, Brazil, China, Saudi Arabia and the United Arab Emirates.

There over 40 sites where EOR has been used to safely and securely store captured CO_2 underground, and continuous monitoring has verified that the wells are intact and secure. There are currently 30 full-scale projects operating globally and 164 new projects in development, with a total storage capacity of 241.6 Mt y^{-1}. These facilities have demonstrated that million-tonne CO_2 injection rates at multimillion-tonne storage sites are possible. Importantly, monitoring confirms that all the CO_2 injected is ultimately stored. This monitoring has laid the foundation for CCS to become a critical climate change technology (GCCSI 2022).

5.2.3.2 Victorian Research Context

In Victoria, oil is produced in fields located offshore in the Gippsland Basin, as shown in Figure 29 below. The Gippsland Basin is a world class oil reserve that has produced about 90% of Australia's

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[46] IEA Greenhouse Gas R&D Programme (2009).

crude oil. Recoverable reserves of existing fields are estimated at 3,861 million barrels (IEA Greenhouse Gas R&D Programme, 2009).

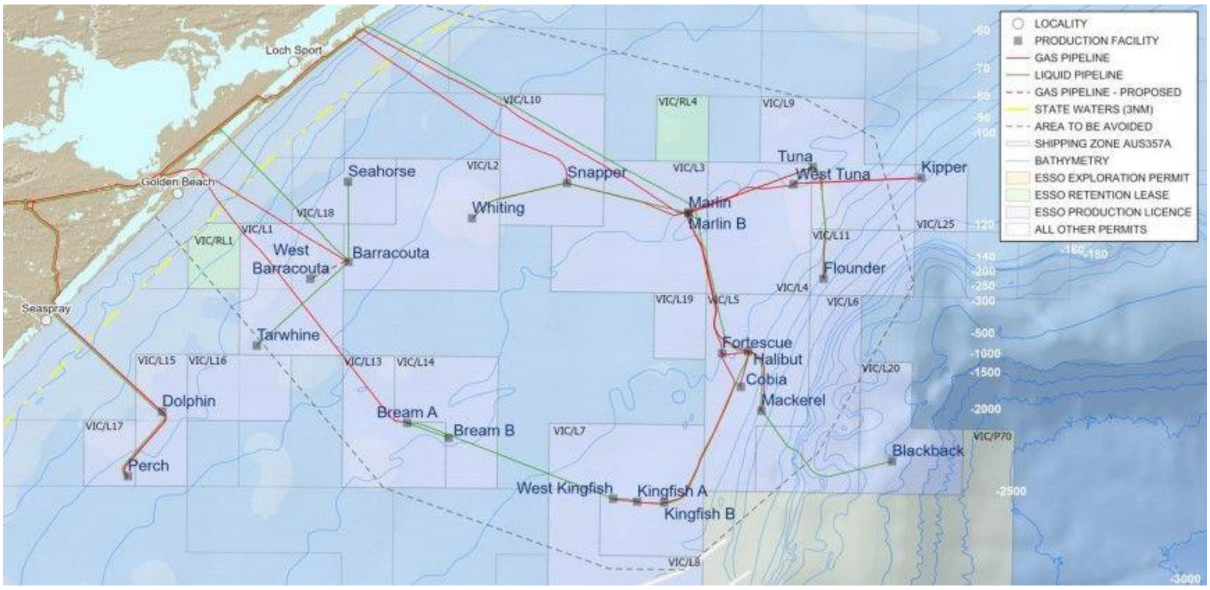

Figure 29: *Gippsland Basin showing ExxonMobil oil and gas fields*[47]

Oil in the Gippsland Basin occurs within the sediments of the Latrobe Group. This reservoir is highly permeable and has excellent properties for conventional oil recovery. It has been estimated that it would be technically feasible to recover 1,286 million barrels of oil from the Gippsland Basin using EOR (IEA Greenhouse Gas R&D Programme 2009). However, it is expected that the level of oil saturation at the end of conventional extraction is likely to be too low to make EOR an economically feasible proposition (Njongwe 1984).

The oil and gas fields are approaching the end of their working lives, creating an opportunity to utilise the depleted reservoirs for CO_2 storage. Esso Australia recently announced the South Eastern Australia CCS Hub, which from 2024 will use existing gas extraction infrastructure to store CO_2 in the depleted Bream reservoir, located 46 km offshore in Bass Strait. As Esso's oil and gas fields in Bass Strait reach the end of their working lives, they can be converted to CO_2 storage reservoirs, with potential capacity of 50-300 billion tonnes.[48] In addition, the CarbonNet Project has validated that safe CO_2 storage sites are available in barren strata in the near-offshore region of the Gippsland Basin, with injection capacities in excess of 5 Mt/y.[49] The Gippsland Basin is thus a valuable resource that can support the development of large-scale low-carbon new industries in Victoria.

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[47] https://www.boilingcold.com.au/regulator-blasts-exxonmobils-bass-strait-maintenance-orders-massive-decommissioning-effort/

[48] https://www.exxonmobil.com.au/energy-and-environment/energy-resources/upstream-operations/the-south-east-australia-carbon-capture-hub

[49] https://earthresources.vic.gov.au/projects/carbonnet-project

5.2.3.3 ACI Comments

It is possible that CO_2-EOR may be regarded as a more interesting proposition in the 2030s, when hydrogen is being produced from Victorian lignite and CO_2 is being sequestered in the near-shore Gippsland Basin. The availability of large quantities of compressed CO_2 in the near vicinity may make CO_2-EOR more technically attractive, but ultimately it will depend on the economics of the process, which cannot be anticipated at this time. The characteristics that make the Bass Strait oil fields so valuable, high permeability and porosity, make EOR much less likely as an economic proposition. Esso is in the best position to assess this technology as a commercial opportunity.

6 Biological Conversion of CO_2

Biological conversion of CO_2, using natural organisms such as plants, algae and bacteria, is an effective way to take advantage of complex chemical processes under mild operating conditions. The processes for utilising CO_2 in horticulture, microalgae culture and microbial culture are discussed below. Using this approach, it is possible to recycle CO_2 into useful products such as human and animal foods, fertiliser, ethanol, methane and plastics.

6.1 HORTICULTURE

6.1.1 Current Status

Carbon dioxide (CO_2) is an essential plant nutrient that is metabolised through photosynthesis, the chemical process used by green plants to convert sunlight into the sugars needed for growth and vigour. For the majority of glasshouse crops, net photosynthesis increases as CO_2 levels increase from 340–1,000 ppm (parts per million).

The benefits of CO_2 supplementation on plant growth and production within the glasshouse industry environment have been well understood for many years. Supplementary CO_2 increases productivity through earlier flowering, higher fruit yields, reduced bud abortion in roses, improved stem strength and flower size.

Carbon dioxide can be obtained either by burning carbon-based fuels or directly from tanks of pure CO_2. The most common method is to burn natural gas, propane or liquid fuels in specialised CO_2 generators located throughout the glasshouse. A potential disadvantage of this system is that the heat generated by these units may have a localised effect on temperature and disease incidence. Liquid CO_2 is becoming increasingly popular even though it is usually more expensive. The main advantages of using liquid CO_2 include purity of product, no concerns about crop damage, nor heat or moisture production, better control of CO_2 levels and the flexibility to introduce the CO_2 within the plant canopy at any time (Wang et al. 2022).

Figure 30: *Glasshouses are enriched with CO_2 for improved plant productivity*

The use of glasshouses is a relatively simple way to recycle CO_2 captured from industrial waste gases. In the Netherlands, OCAP (Organic Carbon dioxide for Assimilation of Plants), a joint venture between Linde Gas Benelux and VolkerWessels, has accomplished this at very large scale by taking advantage of a fortuitous combination of circumstances.

OCAP has established a business supplying glasshouses with CO_2 sourced from industrial waste gases. Each year, OCAP sources over 400,000 t CO_2 from the Shell oil refinery at Pernis near Rotterdam, from where it is supplied to over 580 glasshouses via an 85 km long transport pipeline and a ~300 km long distribution network. This arrangement was made possible because Shell Pernis is located within 100 km of the glasshouses it serves, and there was an existing, previously unused pipeline system that fortuitously ran between the suppliers and the glasshouses.[50] Currently this network supplies 2000 ha of glasshouses, but the network could service up to 5000 ha if sufficient CO_2 could be sourced.[51]

OCAP also sources CO_2 from biological industry sources, including Abengoa, a specialist in bioethanol production, and ARN, which ferments vegetable, fruit and garden (VFG) waste. These processes produce bio-CO_2, which is approved by the EU for use in renewable processes. While the quantity of CO_2 currently being sourced from sustainable bio-sources is still modest, it is expected that the rapid growth in the number of biogas processors will boost the availability of bio-CO_2.[52]

Figure 31: *Loading bio-CO_2 from a bioethanol plant*[53]

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[50] https://webcache.googleusercontent.com/search?q=cache:fpg2RLiEgalJ:https://www.the-linde-group.com/en/clean_technology/clean_technology_portfolio/co2_applications/greenhouse_supply/index.html+&cd=2&hl=en&ct=clnk&gl=au

[51] http://www.atlascopco-gap.com/news-downloads/reference-stories/stories-industrial-gases/greenhouse-effect/

[52] https://www.linde.nl/nl/news_and_media/press_releases/linde-ocap-levert-eerste-gecertificeerde-bio-co2-uit-duurzame-biomassa.html

[53] https://www.linde.nl/nl/news_and_media/press_releases/linde-ocap-levert-eerste-gecertificeerde-bio-co2-uit-duurzame-biomassa.html

A project led by DNV GL found that CO_2 from biogas can be contaminated with as many as 60 different chemical compounds, including carbon monoxide, ammonia, sulphur, acids, halogens and organic volatiles. These can potentially have an adverse effect on plant growth and health and safety of greenhouse personnel. After assessing the toxicity of individual components for plants, DNV GL developed a new recommended standard for CO_2 purity from biogas, which is much less stringent than the food-grade CO_2 currently specified in glasshouses (Holstein 2017).

6.1.2 ACI Comments

The use of CO_2 supplementation in glasshouses is well established in commercial practice, so it has a TRL of 9.

The use of CO_2 to boost crop productivity in glasshouses is a low volume, high value way to effectively recycle CO_2. Consumption of any foods produced in this manner will eventually return the CO_2 to the atmosphere, so it is not a permanent sequestration solution. However, residual biomass, such as stems, leaves and roots, could be converted to biochar by pyrolysis, creating an additional product for use as a soil amendment, and stabilising the carbon content in the process. Conversely, the waste biomass could be gasified to be converted to hydrogen with the resultant CO_2 captured and sequestered leading to a net zero or net negative emissions profile.

Glasshouse horticulture is an existing high value business in the Latrobe region. The development of a pipework network to convey recycled CO_2 to existing and new glasshouses would support the expansion of this valuable industry in the area. Additionally, greenhouses are labour intensive and would provide significant employment opportunities at the low and medium skill levels for the Latrobe Valley community.

In 2021, CSIRO, Flavorite Tomatoes in Warragul, and the Japanese company IHI, planned to undertake a feasibility study into the technological and economical requirements of implementing a 200t/d CO_2 capture plant at Loy Yang and supplying CO_2 to local glasshouses. A proposal for funding was submitted to the Victorian Government's Department of Environment, Land, Water and Planning, but did not proceed because IHI withdrew from the project. Given that Flavorite Tomatoes saw potential benefit to its business from using recycled CO_2, there would be value in revisiting a variation of concept with them.

6.2 MICROALGAE CULTURE

6.2.1 Current Status

Microalgae are single-celled primitive plants that are ubiquitous in fresh, brackish and marine waters worldwide. The promise of microalgae is that some strains can accumulate as much as 50% of their mass as lipids or oils, which can be extracted and upgraded to biodiesel, and have a shorter cultivation time than conventional oil producing terrestrial plants. Microalgae also contain valuable natural chemicals including omega-3 fatty acids and pigments (Ghosh et al. 2016).

Production of valuable products by microalgae culture has offered great promise, due to its advantages over terrestrial crops - the solar light photoconversion efficiency and growth rate are higher, arable land is not required, herbicides and pesticides are not needed, and brackish, saline or waste water can be used (Dibendetto et al. 2016).

Microalgae has been the focus of intensive research and development since the oil crisis in the 1970s, which stimulated interest in alternative sources of fuel. In 1978, the Carter Administration established what was then called the Solar Energy Research Institute (SERI) in Golden, Colorado, to investigate alternative sources of natural oil for biodiesel production. This led to the development of large-scale microalgae farms, based on the use of open, shallow ponds in which some source of waste CO_2 could be efficiently injected and captured by the microalgae. The ponds were shallow “raceway” designs, in which the algae, water and nutrients circulated around a racetrack, with paddlewheels driving the flow. They were operated continuously, with water and nutrients constantly fed to the pond while microalgae-containing water being removed at the other end (Sheehan et al. 1998).

Development of large-scale microalgae culture by SERI was terminated in 1996. A subsequent wind-up review of the program concluded that a microalgae biodiesel production system must operate at high efficiency and with minimal inputs at overall low cost. Cost constraints restrict microalgae cultivation systems to the simplest possible devices, which are large unlined, open, mixed raceway ponds. However, the growth rate of microalgae is very slow and the open cultures are susceptible to being overcome by wind-blown predatory species. SERI recommended that the future R&D focus should be on the development of more productive microalgae strains via genetic engineering or other strain improvement methods, to achieve very high solar conversion efficiencies and high oil yields (Sheehan et al. 1998).

Since the late 1990s there has been very little progress in this regard. While there has been some limited commercial success in microalgae culture, notably in the production of natural pigments (astaxanthin and β-carotein) in seawater and omega-3 fatty acids (using strains selected to grow in the dark), the dream of producing biodiesel from microalgae has not been realised. Recent reviews have highlighted the fact that the cost of microalgae culture is still too high (Dębowski et al. 2022; Novoveská et al. 2023), and no significant progress has been made on the improvement of microalgal strains (Ghosh et al. 2016). Closed photobioreactor (PBR) systems have been investigated to overcome the problem of predation (Figure 32), but productivity is limited by the growth of dense biofilms on the reactor surface, reducing light availability (Dębowski et al. 2022). The focus is now beginning to turn toward the development of heterotrophic strains of microalgae that grow in the dark (and do not consume CO_2) for the production of biodiesel (Lowrey et al. 2015) and pigments (Hu et al. 2018).

Figure 32: *Examples of large-scale cultivation of photosynthetic microalgae and cyanobacteria. (a) Open pond (Israel) (photo credit Soren Nielsen) (b) Floating offshore closed PBRs with capacity 8000 L each at Algae Systems (USA) (c) 1000 L pond (Turkey) (d–g) Large-scale 40,000 L tubular PBRs at Akvatek (Turkey).*[54]

Despite the investment of many millions of dollars to develop the potential of microalgae culture, very little progress has been made in overcoming the significant barriers to its commercial success. It seems unlikely that further research efforts will solve these problems in the foreseeable future.[55]

6.2.2 Victorian Research Context

Professor Sandra Kentish at the University of Melbourne, in conjunction with the Peter Cook Centre, is working on a method to reduce the cost of delivering CO_2 as a nutrient to large-scale microalgae culture ponds. The issue is that delivery of a purified and compressed tanker of CO_2 to a microalgae

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[54] Novoveská et al. 2023

[55] https://www.greentechmedia.com/articles/read/lessons-from-the-great-algae-biofuel-bubble#gs.klls7d42

farm includes the energy penalty involved in stripping CO_2 from a scrubber solvent and compression. The idea being pursued by Prof. Kentish is that these costs could be avoided by transporting CO_2-loaded solvent to the microalgae farm, and pumping the solvent through the ponds within hollow fibre or flat sheet membranes, as shown in Figure 33 below.

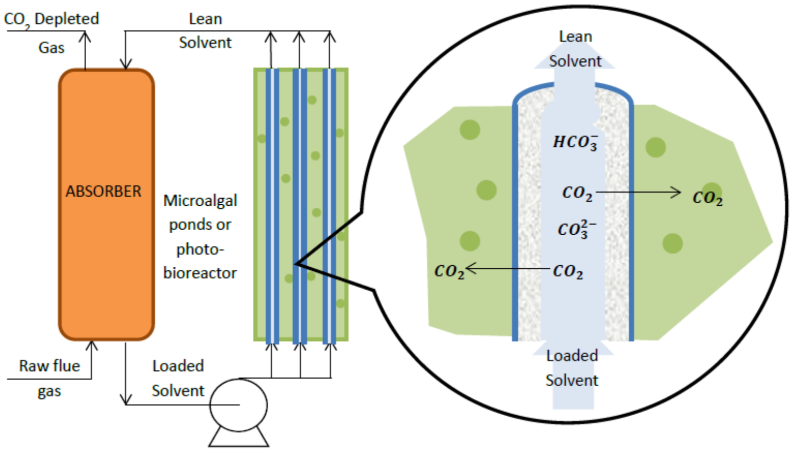

Figure 33: *Microporous membranes desorbing CO_2 from scrubber solvent into microalgae culture*[56]

The membranes are microporous, but are coated with a thin non-porous polymer coating. The CO_2 desorbs directly from the rich solvent through the walls of the membrane and into the microalgae growth medium. The microalgae act effectively to regenerate the solvent, replacing the role of the classical reboiler.

The loaded solvent can be readily piped or even trucked across longer distances for use and then returned in a lean state. It has been shown that the approach works with a range of different solvents (potassium carbonate, monoethanolamine and potassium glycinate) and with five different microalgae species.

Evaluation at bench scale demonstrated that this system can achieve comparable biomass productivity ($0.10\ g\ L^{-1}\ d^{-1}$) to the conventional direct bubbling method, but with a lower energy cost and higher CO_2 utilization efficiency (Xu et al. 2019).

Nominated contact details:

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Email:	sandraek@unimelb.edu.au
Website:	https://findanexpert.unimelb.edu.au/profile/14055-sandra-kentish

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[56] Zheng et al. 2016

6.2.3 ACI Comments

In the limited instances where microalgae culture has been successfully commercialised, it is usually done in areas where there is a high incidence of sunlight, such as Western Australia (β-carotene production). The Latrobe Valley has a relatively low level of incident radiation, making it a poor choice for microalgae culture.

Given the high level of investment worldwide in microalgae culture, and the poor return in terms of commercial developments, there is no reason to regard this as a lucrative opportunity for the Latrobe Valley.

R&D investment in microalgae culture in Victoria is not recommended.

6.3 MICROBIAL CULTURE

Microbial species such as bacteria, archaea and fungi are ancient forms of life that have adapted to occupy every environmental niche on the planet. This enormous biodiversity presents opportunities to identify species that can effectively utilise CO_2 and convert it into value-added products. This is an area of research that has not been well explored, but some significant opportunities have already been identified.

6.3.1 Methane

6.3.1.1 Current Status

Methane, CH_4, is the major component of biogas, which is produced from biological wastes during the process of anaerobic digestion. Anaerobic digestion is a fermentation process, which takes place in a closed airtight reactor where organic raw materials such as manure, food waste, sewage sludge and organic industrial waste are converted into biogas and solid residue. The produced biogas is a mixture of 50–70 % methane and 30–50 % carbon dioxide and smaller amounts of water vapour, hydrogen sulphide and other minor components. Biogas produced from organic waste streams does not add to the CO_2 load in the atmosphere and is thus a “green” sustainable energy vector. It is anticipated that biogas will play a significant role in shifting to a sustainable decarbonised society.[57]

Anaerobic digestion is a complex process involving a diversity of microorganisms working synergistically. The digestion process begins with bacterial hydrolysis of the input materials in order to break down insoluble organic polymers such as carbohydrates and make them available for other bacteria. Acidogenic bacteria then convert the sugars and amino acids into carbon dioxide, hydrogen, ammonia, and organic acids. Acetogenic bacteria then convert these resulting organic acids into

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[57] https://www.ieabioenergy.com/wp-content/uploads/2018/08/anaerobic-digestion_web_END.pdf

acetic acid, along with additional ammonia, hydrogen, and carbon dioxide. Finally, methanogens convert these products to methane and carbon dioxide.[58]

Anaerobic digestion has recently been proposed as a promising system to biochemically convert captured CO_2 into methane. For example, supplementary injection of CO_2 into a pilot scale food waste digestor was found to increase methane production by 20 % (Bajón Fernández et al. 2015). Similarly, injection of CO_2 into a pilot scale sewage sludge digestor was found to increase methane production by 12 % and improved resilience to temporary overloads (Alibardi et al. 2017).

While these results are preliminary, they point toward a simple way to improve the productivity of biogas digestors using recycled CO_2. Further research is required to demonstrate the feasibility of the concept in a commercial biogas plant.

6.3.1.1.1 Electrochaea GmbH

In Europe, a variant of this concept has been developed by Electrochaea GmbH, which has headquarters in Munich/Germany and an affiliate company in Denmark. Using patented technology originating from the University of Chicago (Mets 2016; Mets 2018), Electrochaea offers a proprietary power-to-gas technology that recycles CO_2 while using excess renewable electricity to produce biological methane that can be stored on the gas grid.

The Electrochaea process utilises a strain of the ancient archaea species *Methanothermobacter thermautotrophicus* (Mets 2016). Electrochaea is currently pursuing energy storage via a two-step power-to-gas system that uses an off-the-shelf electrolyser to produce hydrogen. As shown in Figure 34 below, the hydrogen is then fed to a separate bioreactor containing the archaea along with carbon dioxide from a biogenic or industrial source; the archaea converts the CO_2 and H_2 to methane.

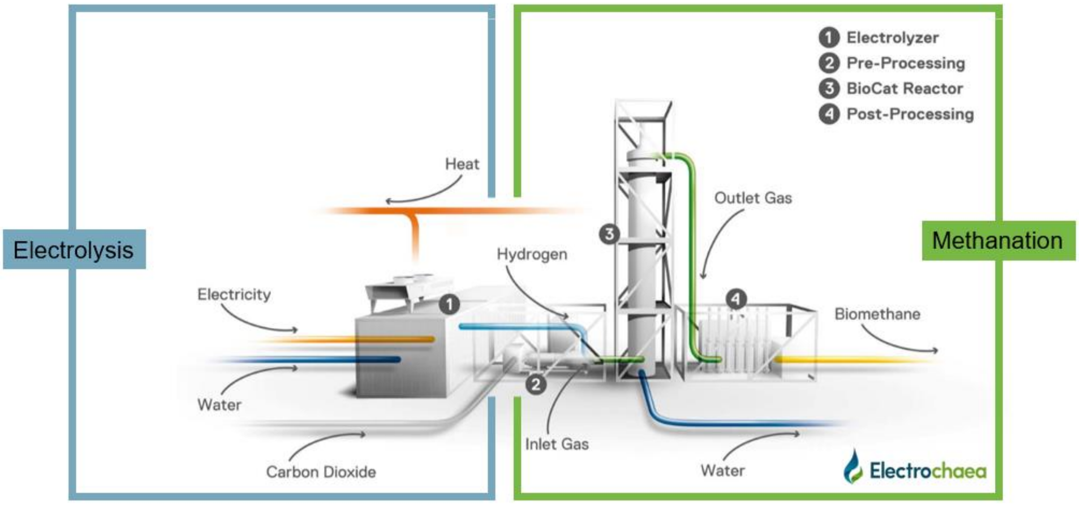

Figure 34: *Electrochaea's power-to-gas process*[59]

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[58] https://www.americanbiogascouncil.org/biogas_what.asp
[59] https://www.electrochaea.com/technology/

Electrochaea's process is anaerobic and operates at 65 °C. The organism is very tolerant of process imbalances, and is very robust to extended stoppages (Hafenbradtl 2017). The archaea is indifferent to the source of CO_2 and can use commonly available sources such as raw biogas from anaerobic digesters, fermentation off-gas from breweries and ethanol plants, and flue gas from combustion processes. The high selectivity of the archaea means that minimal post-reaction gas treatment is needed before the product gas is injected into the gas grid. Oxygen and heat are by-products from the process.[60]

Electrochaea has demonstrated commercial scale power-to-gas technology at its BioCat project in Denmark, shown in Figure 35 below. The system included a commercial scale methanation reactor and balance of plant, an electrolyser, gas polishing system and gas grid injection station, all located at the BIOFOS wastewater treatment facility in Avedøre, near Copenhagen. The system has flexible operational modes and responds rapidly to available energy, so it could also provide frequency regulation services to the Danish power grid. The first grid injection took place in September 2019.[61]

Figure 35: *Electrochaea's BioCat project, Denmark (© Electrochaea)*

In 2020, Electrochaea received funding from the European Innovation Council (EIC). The EIC Accelerator Program project involved a detailed engineering design of a 10 MWe biomethanation plant, which was completed in November 2021. With the completion of the standardized design for a

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[60] https://www.electrochaea.com/technology/

[61] https://www.startup-energy-transition.com/award-finalist-electrochaea-will-disrupt-the-power-storage-market/

10 MWe plant, Electrochaea's multi-patented technology is ready for worldwide commercial development.[62]

6.3.1.2 ACI Comments

The Electrochaea process (TRL 7) would be more difficult to implement, as the microorganisms require an additional supply of hydrogen. Currently, the supply of CO_2-free hydrogen from renewable sources is a limiting factor, but there will likely be an abundance of lignite-derived CO_2-free hydrogen in the Latrobe Valley in coming decades. The techno-economics of methane production by this route are unclear, especially in comparison with catalytic processes (Sabatier reaction) as described in Section 8.3.8. Further work is justified to establish whether there is a niche opportunity for the Electrochaea process in the Latrobe Valley.

6.3.2 Ethanol

6.3.2.1 Current Status

6.3.2.1.1 LanzaTech

LanzaTech, headquartered in Chicago, USA, has developed a bacterial gas-phase fermentation process that converts waste gases containing CO_2 and CO to ethanol. LanzaTech specialises in the culture of gas fermentation bacteria and archaea, to produce a variety of value-added products from waste industrial gas streams. This is quite different to the majority of other fermentation processes, which usually utilise sugars as the energy source. In gas fermentation, C1 gases such as CO and CO_2 are used as the energy source, usually requiring additional hydrogen for metabolism.

LanzaTech's workhorse microbe is *Clostridium autoethanogenum*, which naturally converts CO to ethanol. Four commercial installations based on this process have been installed in China and one in Belgium, with another in India under construction (see Table 6 below).

***Table 6**: Current and near-term markets for products utilising waste CO (Zhu 2023)*

Plant	Location	Status	Start year	Capacity t/y ethanol	CO_2 source
Shaugang Steel	Caofeidian, China	Operational	2018	46,000	Steel mill off-gas
Shougang Jiyuan	NingXia, China	Operational	2021	46,000	Ferroalloy off-gas
NingXia Binze	NingXia, China	Operational	2022	60,000	Ferroalloy off-gas
Guizhou Jinze	Guizhou, China	Operational	2023	60,000	Ferroalloy off-gas
ArcelorMittal Ghent	Ghent, Belgium	Operational	2023	64,000	Steel mill off-gas
IndianOil Corporation	Panipat, India	Under construction	2023	34,000	Refinery off-gas

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[62] https://www.electrochaea.com/technology/

LanzaTech has also developed an extensive IP portfolio around genetic mutation of *Clostridium autoethangenum* for efficient production of other industrial chemicals from CO, such as acetone and isopropanol.[63]

LanzaTech is also pursuing strategies to employ gas fermentation to convert CO_2 to valuable products. It has partnered with Twelve Benefit Corp., which has developed a catalytic membrane system that uses renewable energy to convert CO_2 to CO (Kuhl et al. 2023), which can then be converted to ethanol using LanzaTech's standard process.[64] LanzaTech has also patented a process utilising low temperature reverse water-gas shift reaction (RWGS) to convert CO_2 to CO in the presence of H_2 (Rosin et al. 2023), as well as genetically modified strains of *Clostridium autoethangenum* that can utilise CO_2 directly (Garg & Koepke 2022). The engineered microbes have been demonstrated to directly produce ethylene from CO_2 in a continuous process.[65]

6.3.2.2 Victorian Research Context

As described in Section 8.3.6 below, ethanol is an important fuel and precursor to other critical industrial chemicals, such as ethylene. To be cost-effective, production must be at a very large scale and use an inexpensive feedstock. In the shorter term, the most prospective source of large volumes of CO and H_2 would be syngas produced by gasification of Victorian lignite, as proposed by the HESC project. With appropriate planning and foresight, a local biomass industry could be established, based on industrial hemp or plantation forestry, to provide a renewable feedstock for gasification and thus allowing mass production of renewable ethanol. The ethanol can be readily converted to ethylene, and provide an opportunity for local plastic producer, Qenos, to synthesise 'green' recyclable polyethylene.

From a strictly CO_2 recycling perspective, there are several technology approaches under development for conversion of CO_2 to syngas. CSIRO and RMIT are collaborating to develop a catalytic dry methane reforming process to produce syngas from a mixture of CO_2 and CH_4 (Section 8.3.3.2). Danish company Topsøe's eREACT™ RWGS system can produce syngas from CO_2 and H_2 (Section 8.3.4.1.2), and Sunfire GmbH in Germany sells a process for producing syngas by high temperature SOE co-electrolysis of steam and CO_2 (Section 9.2.1.1.1). Locally, a CSIRO-led consortium is developing a similar SOE-based process (Section 9.2.1.2).

While there is great interest in production of syngas from CO_2 and renewable energy, the available technology is still under development or at a relatively small commercial scale, so the prospect of producing cheap syngas at the scale required for the LanzaTech process is quite distant.

6.3.2.3 ACI Comments

The LanzaTech ethanol process has a TRL of 9. This is a significant technology because it demonstrates the potential of gas fermentation to upgrade simple compounds (CO, H_2) to high value

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[63] https://www.chemistryworld.com/news/reprogrammed-bacterium-turns-carbon-dioxide-into-chemicals-on-industrial-scale/4015307.article
[64] https://www.greencarcongress.com/2022/03/20220304-12.html
[65] https://lanzatech.com/lanzatech-produces-ethylene-from-co2-changing-the-way-we-make-products-today

products using natural microorganisms as biocatalysts. Practically, however, this technology is limited by the availability of a significant source of low-cost or waste CO and H_2 *to make ethanol production viable.*

LanzaTech (and others) have found it challenging to identify natural microbes that can utilise CO_2 *as a carbon source. This is because* CO_2 *is the lowest energy state in the carbon metabolic chain. The common response to this problem is to genetically engineer the microorganism to boost the natural capabilities, which is a strategy being pursued by LanzaTech. While this may be an acceptable solution in some jurisdictions, it is not suitable for implementation in Australia. Here, GMO organisms must be cultivated in a Class 2 biocontainment facility, which is the standard required for pharmaceutical manufacture, with similar attendant costs. This would not be cost-effective for relatively low-value products such as ethanol and other industrial chemicals.*

LanzaTech's non-GMO alternative, using an external source of H_2 *and RWGS to upgrade* CO_2 *to CO, is a more practical approach, but the economics are then dependent on securing a low-cost source of hydrogen.*

6.3.3 Biomass / Edible Protein

6.3.3.1 Current Status

Commercial interest in production of human food by gas fermentation had its origins in a NASA-funded program to develop a life-support system for astronauts in space. Efforts were focused in automated continuous culture of the bacterium *Cupriavidus necator* (then known as *Hydrogenomonas eutropha*), grown on oxygen (O_2) and hydrogen (H_2) generated by electrolysis of water, and carbon dioxide (CO_2) recovered by the air purification system. The harvested cellular material was to be used as a source of food for the astronauts (Foster & Litchfield 1964).

In the 1970s, *C. necator* (then known as *Alcaligenes eutrophus*) was evaluated by Imperial Chemical Industries (ICI) as a candidate for industrial single cell protein production, as animal feed and for human consumption. However, it was soon found that *C. necator* synthesized large quantities of poly (3-hydroxybutyrate) biopolymer (PHB). This led to the development of a new range of products, known as BIOPOL, based on cultivation of *C. necator* on glucose. However, the viability of the product was plagued by high cost and formulation difficulties, and the business was ultimately shut down in 2012 due to uncompetitive production costs (Liggat 2019). The IP rights were subsequently acquired by a South Korean company, CJ Cheiljedang, which is continuing development of an improved process that uses recombinant *E. coli* strains expressing *C. necator's* PHB biosynthesis genes (Raberg et al. 2018).

Gas-phase cultivation of *C. necator* for PHB production was first investigated by Japanese researchers. *C. necator* requires oxygen for growth which, along with the supplied H_2, is potentially explosive. To manage this safely, the fermentation system was designed to operate below the explosive limit, by controlling the gas pressures and recycling off-gases for maximum utilisation (Tanaka et al. 1995). These researchers found that safe operation under autotrophic conditions meant that cell growth during the first phase was limited by oxygen supply, so subsequent research focused on a combination of heterotrophic and autotrophic conditions, in which acetic acid was used as the carbon source during the growth phase (Sugimoto et al. 1999; Ishizaki et al. 2001).

A similar approach was pursued by researchers at the Flemish Institute for Technological Research (VITO), who have replicated and extended the earlier work (Garcia-Gonzalez et al. 2015; Garcia-Gonzalez & De Wever 2018). It was recently reported that *C. necator* cells can be grown on CO_2 and H_2 alone, under O_2 control, producing 13 g/l biomass containing 80% PHB (Lambauer & Kratzer 2022).

In 2009, Oakbio Inc., of Sunnyvale, California, was formed to investigate production of PHB using CO_2 and H_2 as feedstocks (Sefton & Coleman 2019). Finding that autotrophic production of biomass was easier than production of PHB, in 2017 the company name was changed to NovoNutrients to coincide with the release of a range of microbial biomass products for the animal and aquafeed markets. NovoMeal is a nutritionally balanced, low cost, bulk fishmeal replacement. NovoCeuticals are specialty additives containing essential vitamins, minerals and nutrients for the animal and aqua feed markets.[66] *C. necator* is the main bacterial strain used, but a consortium of other species is included to tailor the amino acid composition of the product (Sefton & Coleman 2019).

More recently, NovoNutrients became serious about producing protein for the human food industry. In April 2023, NovoNutrients announced the signing of a technology development agreement with the Australian company Woodside Energy, to provide funding for construction and operation of a pilot-scale system to deliver larger product samples for market evaluation.[67] Commercial-scale production is expected to begin by mid-decade.[68]

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[66] https://www.oakbio.com/animal-feed/

[67] https://flat-staircase-4fb.notion.site/Woodside-NovoNutrients-Press-Release-TechCrunch-Article-a2d477291fe84783a9eed0b813689a9d

[68] https://www.foodengineeringmag.com/articles/100096-how-novonutrients-upcycles-co2-into-alternative-proteins-for-human-and-animal-food

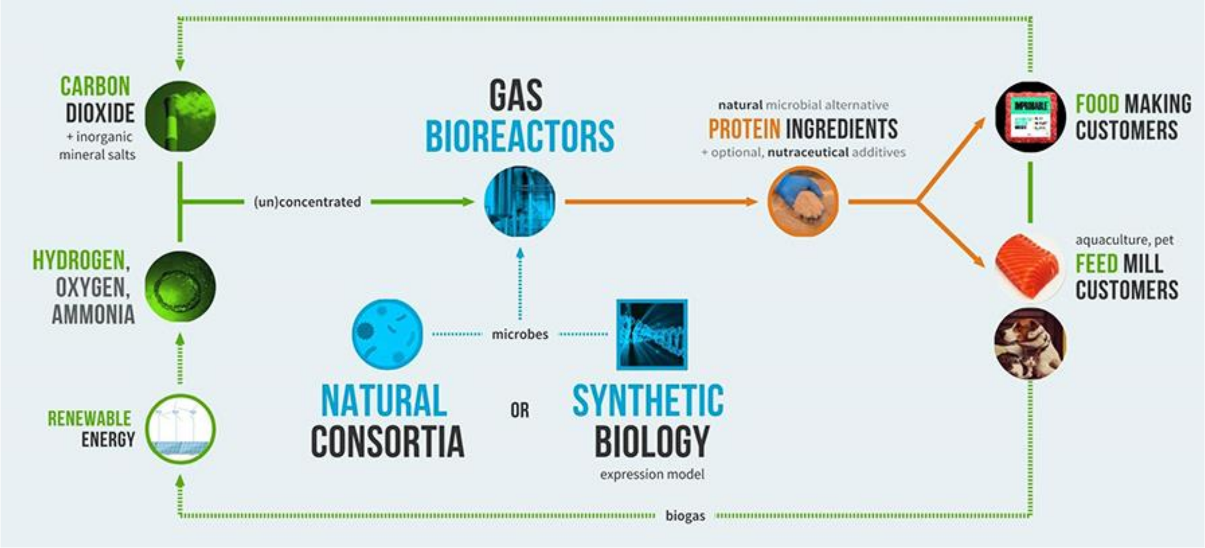

Figure 36: *NovoNutrients' core circular value chain: Inputs (green, left) are captured and fed to microbes in specialized bioreactors (blue), which then ferment those nutrients into protein (orange) destined for food and feed products (green, right). Emissions from food production can then be recirculated into the bioreactors.*[69]

Similarly, Kiverdi, Inc., from Hayward, California, founded in 2011, is developing a process utilising hydrogen-oxidising bacteria to convert CO_2 into microbial biomass for use as animal and human foods. It is developing a product called CO_2 Aquafeed for the aquaculture market, and a human food-grade product called Air Protein as a meat substitute. The CO_2 Aquafeed product is currently at pilot scale, converting CO_2 from a natural gas power plant into aquaculture feed for evaluation in fish feeding trials.[70] Air Protein is still at the developmental stage, with a range of culinary techniques (e.g., cooking, cracking, and fermenting) being investigated to vary the flavour, taste, texture, and nutritional attributes.[71]

In Finland, Solar Foods is a start-up company that is pilot testing a process to produce 'Neo-Carbon' food protein, using hydrogen-oxidising bacteria, direct air-captured CO_2 and H_2 generated by *in-situ* water electrolysis and renewable energy (Ruuskanen et al. 2021).

6.3.3.2 Victorian Research Context

There is currently no research being undertaken on hydrogen-oxidising bacteria production in Victoria or Australia.

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[69] https://www.foodengineeringmag.com/articles/100096-how-novonutrients-upcycles-co2-into-alternative-proteins-for-human-and-animal-food
[70] https://thefishsite.com/articles/capturing-carbon-for-the-aquafeed-sector
[71] https://www.airprotein.com/faq-and-resources

6.3.3.3 ACI Comments

Both NovoNutrients and Kiverdi are developing patent portfolios around uses for the biomass produced by culture of hydrogen-oxidising bacteria, particularly as animal feeds, soil conditioners and plant fertilisers.

It is relevant to note that there is a growing world demand for a protein-rich diet, which cannot sustainably be supported through agricultural means alone. The biomass from hydrogen-oxidising bacteria can be processed into high quality protein, which could be further upgraded to a variety of food products, for both human and animal consumption. Using this process to convert waste CO_2 into valuable food products would seem to have huge potential, and is worthy of further investigation.

7 Inorganic Carbonation

Inorganic carbonation (sometimes also called mineral carbonation) refers to the reaction between CO_2 and certain minerals to form solid precipitates that lead to weathering of the rock. Inorganic carbonation aims to mimic the natural weathering process, where calcium (Ca) or magnesium (Mg) minerals are bound with either CO_2 gas or aqueous CO_2 to form environmentally benign and stable calcium/magnesium carbonates:

$$(Ca,Mg)SiO_{3(s)} + CO_{2(g)} \rightarrow (Ca,Mg)CO_{3(s)} + SiO_{2(s)} + Heat$$

The resulting carbonate minerals are stable over geological time, with about half of the total carbon in the lithosphere being in the form of limestone ($CaCO_3$) and other types of carbonates (Sanna et al. 2014). The large abundance of silicate minerals around the world has led to much research into applications of inorganic carbonation.

Figure 37 below gives a broad summary of the main inorganic carbonation strategies that have been investigated. In this report, the approach taken is to consider these strategies in two broad classes: (i) carbonation of minerals as a form of permanent CO_2 sequestration, and (ii) carbonation of minerals to produce value-added products. This distinction is not clear-cut, but rather tends to reflect a progression of thinking over time.

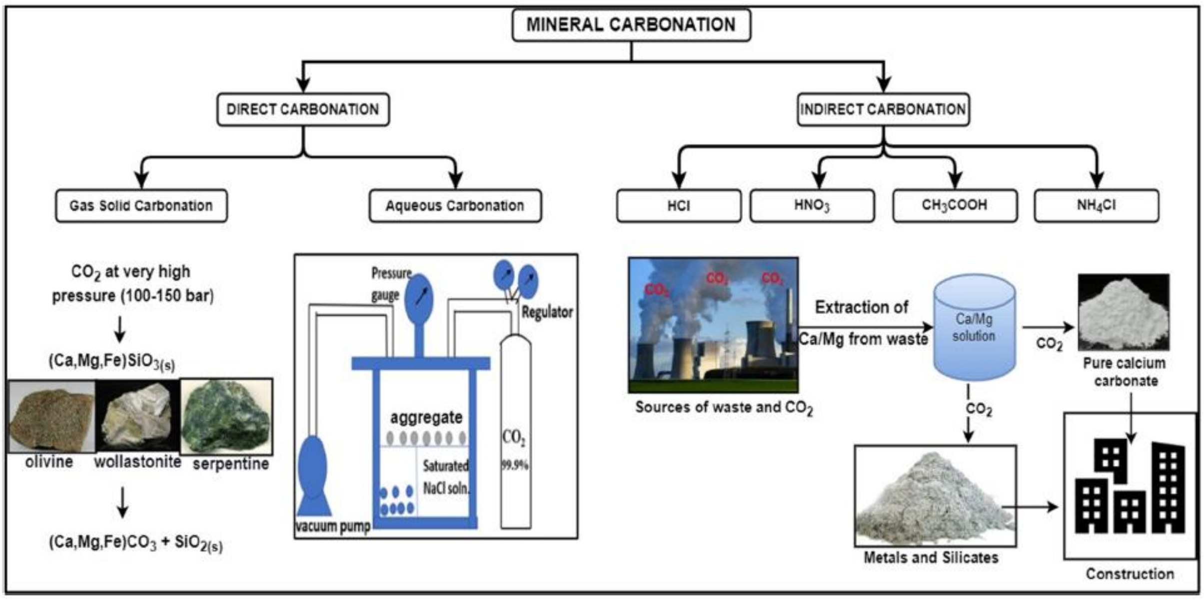

Figure 37: *Pathways of inorganic / mineral carbonation (Hanifa et al. 2023)*

Early interest in this area was to use accelerated mineral carbonation as a form of CO_2 sequestration. The attraction of employing mineral carbonisation for CO_2 sequestration is that it represents an environmentally benign and virtually permanent way to trap CO_2 without the need for post-storage surveillance and monitoring (Sipilä et al. 2008).

There are two main ways in which mineral carbonation can be used for CO_2 sequestration. One is *in situ* carbonation, in which CO_2 is injected directly into natural geological structures to react with the minerals present. Currently, the only example of mineral carbonation being used for geological CO_2 sequestration is the CarbFix Project, which has been operating since 2014 at the Hellisheidi Power Plant in Iceland. Captured CO_2 from the power station is injected into fractured, hydrothermally altered basalts at a depth of 750 m where the temperature exceeds 250 ^{o}C (Clark et al. 2020). The current injection rate is 19.2 t/d, with 96,209 tonnes CO_2 having been stored since 2014.[72] Over 60% of the injected carbon is fixed as carbonate minerals within four months of its injection (Clark et al. 2020).

The second approach is *ex situ* carbonation, in which CO_2 is reacted with finely dispersed mined silicate minerals (e.g., serpentine $Mg_3Si_2(OH)_4$, olivine Mg_2SiO_4, wollastonite $CaSiO_3$) or a range of industrial waste materials e.g. cement waste, ironmaking slag, fly ash, incineration waste and paper mill waste. This process is being actively developed in NSW by Mineral Carbonation International (MCI), a joint venture between Newcastle Innovation (the University of Newcastle's technology transfer company), Orica and GreenMag Group. MCI has developed a process in which serpeninite rock is activated by fine grinding and thermal treatment, and then used to capture CO_2 and produce precipitated magnesium carbonate (Benhelal et al. 2019). MCI is currently constructing a demonstration plant at Orica's Kooragang Island manufacturing site in Newcastle, which will capture 1000-3000 t/y CO_2 from Orica's operations and stored permanently in building materials and other value-added products.[73]

In Western Australia, Alcoa Australia uses mineral carbonation for remediation of red mud waste at its Kwinana alumina refinery. Red mud is the alkaline slurry residue remaining after treatment of bauxite ore in the Bayer alumina process. CO_2 in flue gas is used to generate a hot bicarbonate solution, which is used to neutralise the red mud (Cooling et al. 2005), consuming 35 kg CO_2 per tonne of residue. While this is insufficient to consume all the CO_2 produced in Alcoa's alumina production, direct carbonation of the red mud residue reduces greenhouse gas emissions at the site by more than 70,000 t/y CO_2 (GCCSI & Parsons Brinckerhoff 2011).

The need for fast and nearly complete carbonation of the mineral feedstock during *ex-situ* carbonation efforts has led to research into industrial methods to rapidly and efficiently carbonate various mafic/ultramafic rocks or minerals. Such efforts have included increasing temperature, the addition of aqueous additives, thermal activation of the mineral, and ultrafine grinding of the feedstock minerals (Sanna et al. 2014). However, it seems unlikely that ex-situ mineral carbonation can be made economically viable for mitigation of greenhouse gas emissions. The reaction rates are too slow, and the material flows involved are daunting (2.5-3 tonnes of magnesium silicate mineral is required for each tonne of CO_2 sequestered) (Burgess et al. 2011). The US Department of Energy estimated that ~55,000 tons of mineral feedstock would be needed to carbonate the daily CO_2 emissions from a 1 GW, coal-fired power plant (Gerdemann et al. 2007). In any event, Victoria does not have an adequate supply of suitable magnesium silicate minerals, and the cost of interstate transport would be

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[72] https://www.carbfix.com

[73] https://www.mineralcarbonation.com/mci-carbon-plant

prohibitive, so processes for direct mineral carbonation (e.g. MCI) are not considered further in this report.

Alternative efforts to address the challenge of mineral carbonation have led to a focus on using a range of readily-accessible materials, including certain industrial wastes, where less pre-processing is required and reaction rates are higher. Also, to try to offset the costs associated with CO_2 sequestration, the focus has shifted toward producing marketable products via carbonation, such as ‘green’ construction materials and carbonate chemicals (i.e., calcium carbonate, magnesium carbonate and sodium carbonates).

The following subsections are organised to reflect the types of products and commercial processes that have been developed through these efforts. Unfortunately, there is some overlap between sections in terms of the chemical reactions involved, but the thing that they all have in common is that the chemical reactions occur spontaneously without any external heat input.

The aim here is to emphasise that there are numerous ways that this simple chemistry can be employed, and that the companies taking the lead in this field are reaching commercial success with large potential markets. This is an active area of development internationally, so a final summary subsection is included to extract the relevant learnings and highlight the potential opportunities for development in Victoria.

7.1 CARBONATION FOR PRODUCTION OF ‘GREEN’ CONSTRUCTION MATERIALS

This section considers carbonation of minerals as an opportunity to recycle CO_2 into low-emissions construction materials. Concrete is the second most used substance on the planet after water, with 2.6 billion t/y Portland cement being used in the construction industry. Current production of Portland cement accounts for up to 5-8 % of worldwide industrial CO_2 emissions. The huge environmental significance of concrete use makes the development of ‘greener’ alternatives a high priority worldwide.

7.1.1 Direct Carbonation for Cement and Concrete Products

7.1.1.1 Calera Corporation / Fortera Corporation

Calera Corporation (Moss Landing, California) developed a process to capture CO_2 in the form of carbonates by reacting flue gas with a source of calcium or magnesium ions under alkaline conditions (Constantz et al. 2011). This process, known as “Mineralization via Aqueous Precipitation” (MAP), is shown in Figure 38 below.

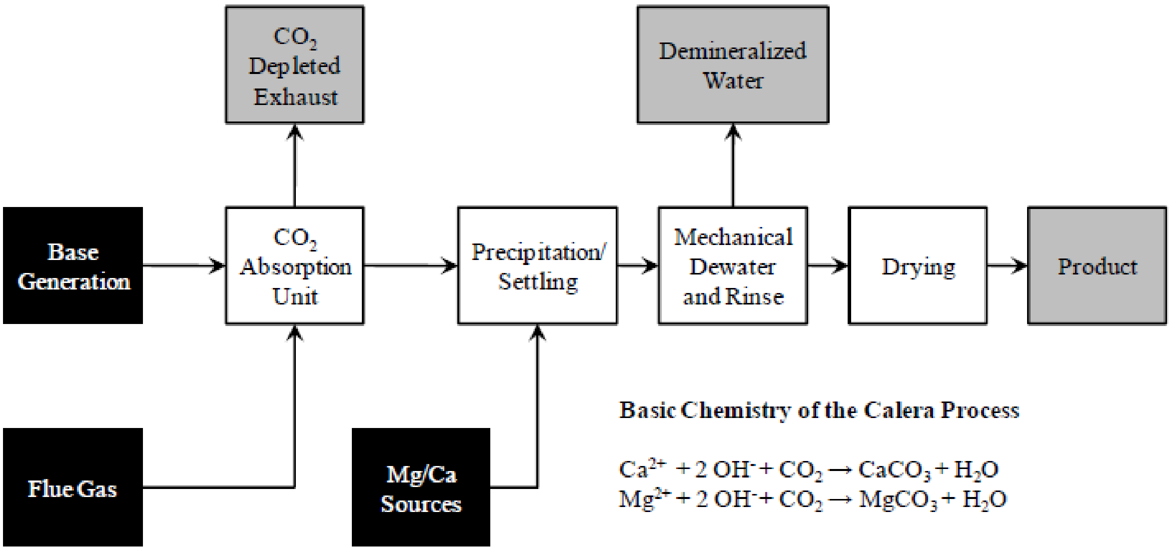

Figure 38: *Calera "Mineralization via Aqueous Precipitation" process (Zaelke et al. 2011)*

The key to the MAP process is the availability of suitable Ca- or Mg-rich brines to react with the CO_2. Desalination reject brines and a variety of industrial waste streams would be suitable. The Calera process is only suitable when flue gas and a suitable brine are available in close proximity. Ideally, the brine should also be alkaline, to enhance the amount of CO_2 that can be captured. The precipitated carbonate is recovered and dried using waste heat from the flue gas.

For sites that do not have sufficient quantity or quality of alkaline brine resources, Calera has a patented electrochemical process called "Alkalinity Based on Low Energy" (ABLE) with the potential to generate caustic soda with low energy requirement. The ABLE electrochemistry process uses a three-compartment membrane cell configuration to electrolyse NaCl to NaOH and to HCl (not to chlorine gas). ABLE was jointly developed and taken to pilot scale under a partnership with the Italian firm Industrie de Nora, a leading supplier of specialised electrochemical cells, membranes and electrodes (Zaelke et al. 2011).

The Calera process generates novel metastable carbonate minerals that have cementitious characteristics when mixed into concrete or with water. These novel carbonate "polymorphs" are produced via control of the precipitation process and are, unlike mined limestone, inherently reactive with Portland cement and harden in the presence of water (Zaelke et al. 2011).

Calera has designed, constructed and operated two pilot plants to develop its CO_2 capture and conversion technologies. These pilot plants produced up to 2 tonnes/day of calcium carbonate using raw flue gas with no concentration of CO_2 needed.[74]

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[74] http://www.calera.com/beneficial-reuse-of-co2/scale-up.html

Calera has demonstrated that its product can be used as a partial replacement for Portland cement (Monteiro et al. 2013). A 20% replacement in blended cement satisfied performance standards for setting behaviour, flow characteristics, and compressive strength (Zaelke et al. 2011). Calera has demonstrated the ability to make a variety of decorative concrete products such as countertops, plant holders and benches. It has also produced full fibre cement board sheets on a commercial line, exceeding strength requirements with formulations that are lighter weight than many existing cement board products (Constantz et al. 2010; Eric et al. 2014).

During 2009-10, Calera actively investigated the potential of installing a demonstration of its MAP process in the Latrobe Valley. However, it found that the local brines available in the Latrobe Valley were unsuitable, so this project was not pursued further (Zaelke et al. 2011).

In 2019 the company adopted a different approach and changed its name to Fortera Corporation. The modified process, now known as ReCarb™, uses calcined limestone as a source of CaO.[75] In 2022, Fortera began building a 15,000 t/y plant to produce ReCarb™ at CalPortland's Redding cement plant in California. The commercial-scale plant will convert 1 t of limestone into 1 t of ReCarb™ by capturing and mineralising CO_2 from the cement plant's kiln. This will result in cement from the plant emitting 60% less CO_2 than ordinary Portland cement.[76]

7.1.1.2 Blue Planet Ltd

Blue Planet was established by Prof. Brent Constantz, the inventor of the Calera MAP process, as a vehicle for commercialisation of a second generation of the technology. The main difference is that the Blue Planet process uses a regenerable ammonia solution as a source of alkali, which avoids the need for an additional electrochemical device (Constantz et al. 2021). A flowsheet of the process is shown in Figure 39 below.

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[75] https://forteraglobal.com/how-we-do-it/

[76] https://www.globalcement.com/news/item/15988-fortera-continues-construction-of-low-carbon-cementitious-material-plant-at-calportland-s-redding-cement-plant

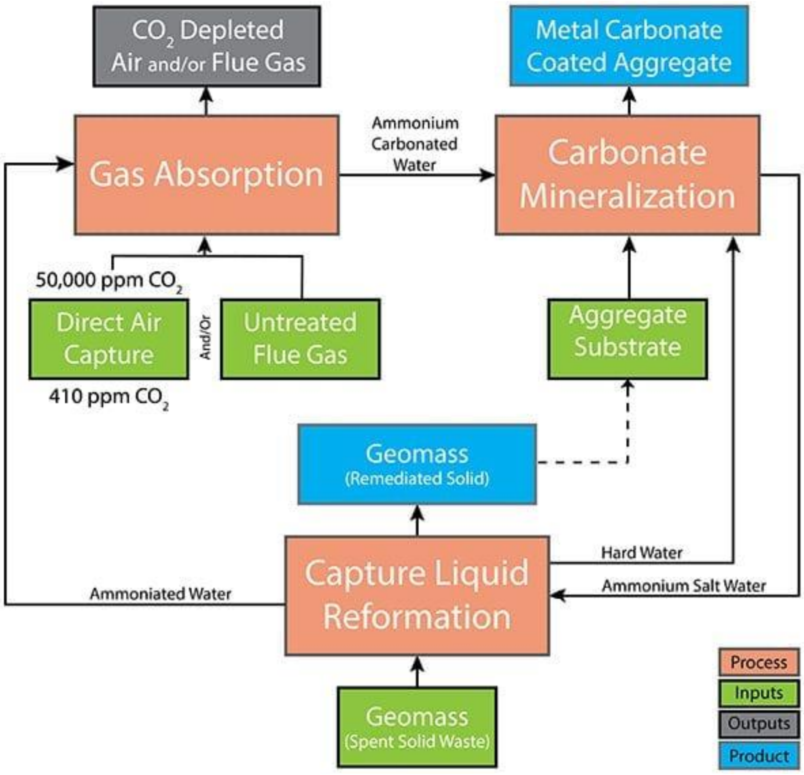

Figure 39: *Blue Planet mineral carbonation conceptual flowsheet © Blue Planet*[77]

In the Gas Absorption section, CO_2 reacts with ammonia to form ammonium bicarbonate:

$$CO_2 + NH_3 + H_2O \rightleftharpoons NH_4HCO_3$$

In the Carbonate Mineralization section, the ammonium bicarbonate reacts with calcium ions to form a precipitate of calcium carbonate, with release of a portion of the captured CO_2:

$$CaCl_2 + 2\ NH_4HCO_3 \rightarrow CaCO_3 + 2\ NH_4Cl + CO_2 + H_2O$$

In the Capture Liquid Reformation section, ammonium ions dissolve calcium from geomass particles, regenerating ammonia:

$$2\ NH_4HCO_3 + \text{Geomass} \rightleftharpoons NH_3 + \text{Hard water}$$

The calcium source, referred to as Geomass, can be a range of materials, including demolished/returned concrete, cement kiln dust, steel slag, fly ash, bauxite residue, or silicate rocks.

The $CaCO_3$ aggregate product is a form of synthetic limestone. Each 100 kg of aggregate contains 44 kg of sequestered CO_2. Once the “carbon costs” of the production process are counted, the net CO_2 sequestered in the aggregate is 40%, or 40 kg in 100 kg of aggregate.

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[77] https://asknature.org/innovation/scalable-carbon-sequestration-inspired-by-the-common-stony-coral/

Blue Planet aggregate is promoted for use in concrete production. It has been tested extensively to ASTM performance specifications, and has been shown to perform comparably or better than existing materials. Concrete produced using Blue Planet aggregate is claimed to be carbon negative, with significant environmental benefits.[78]

7.1.1.3 Carbon8 Systems Ltd

Carbon8 Systems Ltd, based at the University of Greenwich, UK, has developed a process for making a synthetic aggregate by accelerated mineral carbonation of low-grade solids containing CO_2-reactive calcium or magnesium, e.g., limestone fines, paper sludge combustion fines, pulverised fuel ash, cement kiln dust, “out-of-date” Portland cement, etc. (Hills & Carey 2007). The process involves a rotary drum pelletiser, to form the aggregate pellets, followed by carbonation in a curing chamber, as shown in Figure 40 below.

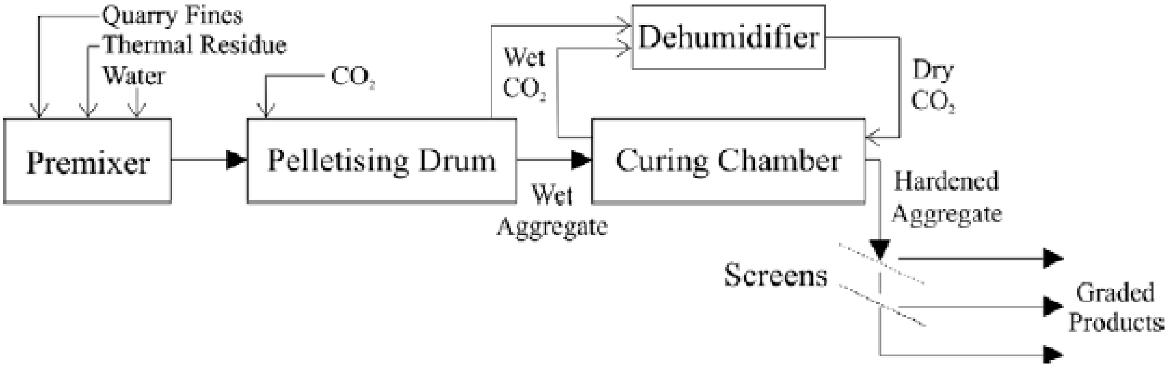

Figure 40: *Carbon8 Systems process for producing carbonated aggregate pellets (Gunning et al. 2009)*

Pilot scale trials were successfully conducted with a range of waste materials, including biomass ash, cement bypass and kiln dusts, municipal waste incineration bottom and fly ashes from two different incinerators, four paper ashes from separate mills, pulverised fuel ash, sewage sludge ash and wood ash. The typical appearance of the aggregates is shown in Figure 41 below.

Figure 41: *Carbonated pellet from paper ash (Gunning et al. 2009)*

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[78] https://www.blueplanetsystems.com/products

The aggregates produced had a bulk density below 1000 kg/m^3 and a high water absorption capacity. Aggregate crushing strengths were between 30 % and 90 % stronger than a commercial lightweight expanded clay aggregate. Cast concrete blocks containing the carbonated aggregate achieved strengths of 24 MPa, making them suitable for use with concrete exposed to non-aggressive service environments (Gunning et al. 2009).

Carbon8 Systems has successfully commercialised its carbonated aggregate product, after a difficult and complex process to demonstrate that its process created a safe usable product from hazardous waste feedstock. In early 2012, a bespoke commercial plant was commissioned at Brandon in Suffolk, UK, producing carbonated lightweight aggregate from municipal solid waste incineration (MSWI) air pollution control residues (APCR). In 2014, a second production line was added to the Brandon facility, increasing its capacity to 60,000 tonnes/y using 30,000 tonnes/y APCR (Gunning & Hills 2015). A second plant was commissioned in Avonmouth in 2016,[79] and a third plant in Leeds in 2018.[80]

The carbonated aggregates were rigorously tested and granted ‘end-of-waste’ designation by the UK Environment Agency. The aggregate material is carbon negative as it contains more imbibed carbon than is generated by its production. Consequently, concrete construction blocks produced are also carbon negative (Gunning & Hills 2015).

Carbon8 is currently working with partners in trials for the use of its aggregate, called CircaBuild, in construction applications, including concrete blocks. In July 2023, CCP Building Products, part of the SigmaRoc group and a large manufacturer and leading supplier of concrete blocks in the UK, announced that the first trials using their Greenbloc Technology and Carbon8’s CircaBuild aggregate resulted in the production of cement-free carbon-negative concrete blocks.[81]

7.1.1.4 Victorian Research Context

Australian Paper is currently investigating the feasibility of installing a waste-to-energy plant at Maryvale in the Latrobe Valley. If implemented, this process would produce an alkali ash waste stream suitable for carbonation.

7.1.1.5 ACI Comments

Accelerated carbonation has the potential to improve the environmental credentials of any new waste-to-energy plant in Victoria. It could help to reduce the greenhouse gas emissions from the plant, while recycling the CO$_2$ to improve the properties of the solid waste, making it safer for disposal to landfill.

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[79] http://c8s.co.uk/carbon8-aggregates/

[80] https://www.aggbusiness.com/feature/ml-s-lighter-aggregate-footprint

[81] https://www.carbon8.co.uk/news/successful-trials-developing-cement-free-carbon-negative-concrete-carbon8s-circabuild-aggregate

For example, the process developed by Carbon8 Systems could potentially allow the waste solids from a waste-to-energy plant to be diverted from landfill and instead converted into an aggregate suitable for use in construction materials or possibly roadmaking.

7.1.2 Direct Carbonation of Fly Ash

7.1.2.1 Value adding of fly ash

Fly ash is a by-product of burning pulverized coal for electricity production. Specifically, it is the unburned residue that is extracted from the flue gas by filtration or electrostatic separation. Fly ash is of interest to this discussion for two reasons: (i) it may contain significant levels of calcium and thus be capable of mineralising CO_2, and (ii) it contains alumino-silicate compounds that can react chemically with calcium hydroxide (e.g. from lime or cement) in the presence of water to form insoluble compounds possessing cementitious properties.[82] This means that fly ash can potentially be used to mineralise CO_2 and be fabricated into useful concrete products, permanently sequestering the captured CO_2 from the atmosphere.

Historically, fly ash has been used as a supplementary cementitious material in concrete at levels ranging from 15 % to 25 % by mass. Fly Ash is sold commercially for use in:

- pre-mixed concrete
- stabilised road base
- roller compacted concrete pavements
- concrete sub-base
- conventional concrete pavements
- roller constructed concrete dams
- concrete products.

Fly Ash can also be used as a filler in the manufacturing of many products, e.g. asphalt, rubber and other manufactured products.[83]

7.1.2.2 Composition of fly ash

In general, the components of fly ash typically include SiO_2, Al_2O_3, CaO/MgO and Fe_2O_3, in the form of amorphous crystalline oxides or various minerals. Fly ash usually contains other trace metal elements, such as Ti, V, Cr, Mn, Co, As, Sr, Mo, Pb and Hg, which may be present at hazardous levels (Zhuang et al. 2016).

According to the American Society for Testing and Materials standard C618, fly ash can be classified as Class C and Class F types based on their calcium oxide contents. Class C (high calcium, >20 wt.%

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[82] https://www.cement.org/docs/default-source/fc_concrete_technology/is548-optimizing-the-use-of-fly-ash-concrete.pdf

[83] https://www.boral.com.au/sites/default/files/media_library/documents/4B0105035_FlyASh_W.pdf

CaO) fly ash is produced by the combustion of lignite and sub-bituminous coals, while Class F (low calcium, <10 wt.% CaO) fly ash is derived from anthracite and bituminous coals (Zhuang et al. 2016).

The composition of fly ash derived from the three main lignite mines in the Latrobe Valley is shown in Table 7 below. It can be seen that there are distinct differences between the three locations. Fly ash from Yallourn and Loy Yang are rich in alumina-silicates but low in Ca and Mg. Fly ash from Morwell is poor in aluminosilicates but rich in Ca and Mg. Fly ash from Yallourn is particularly rich in iron.

Table 7: *Composition of fly ash produced in the Latrobe Valley (% of total ash)*[84]

Component	Yallourn	Loy Yang	Morwell
SiO_2	14.3	16.0	5.8
Al_2O_3	6.7	20.0	3.3
K_2O	0.5	<0.5	0.3
TiO_2	0.5	<0.5	<0.2
$Fe_{(total)}$	25.2	4.0	8.8
Ca	5.7	4.0	22.5
Mg	9.5	7.0	12.9

The fly ash produced from Victorian lignite does not fall neatly into the definitions of Class C or Class F fly ashes. Hence, Victorian lignite fly ashes cannot be classified as either Class F or Class C (Dirgantara et al. 2017).

Worldwide, there has been considerable interest in the potential of Class C fly ash as a mineralisation resource for sequestration of CO_2, including research on Victorian lignite fly ash (e.g., Ukwattage et al. 2015; Hosseini et al. 2016; Yu et al. 2018). This research has been reviewed elsewhere (Wee 2013; Ji & Yu 2018) and is not the focus of this report. It is important to note though, that the qualities of Class C fly ash as a cementitious material are generally improved by carbonation. This will be brought out in the discussion that follows.

7.1.2.3 Carbonation of fly ash

Carbonation of fly ash involves the reaction of CO_2 with the calcium and magnesium present in the fly ash. These elements are not readily accessible, being bound in the form of various mineral phases. As a result, direct carbonation by contact of CO_2 with dry fly ash is not very effective. The rate of carbonation increases in the presence of added water, which helps to solubilise calcium and magnesium ions from the solid matrix of fly ash. Carbon dioxide reacts with these ions to form a layer of carbonate solids on the surface of the particles and filling the small pores, creating a passivating layer. Figure 42 below shows the appearance of Victorian lignite fly ash before and after carbonation.

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[84] Brockway et al. 1991

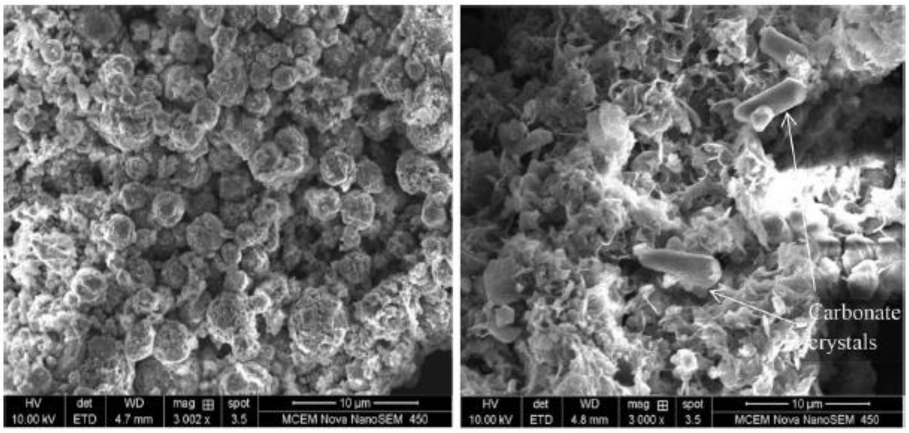

Figure 42: *SEM images of uncarbonated and carbonated lignite fly ash (Ukwattage et al. 2015)*

The carbonation treatment effectively coats the surface of fly ash and blocks the pores, locking in the heavy metals and reducing or preventing their leaching (Wee 2013; Ji & Yu 2018). In addition, fine calcium carbonate crystals precipitate on the surface. These provide a favourable surface for nucleation and growth of hydration products in cement/concrete, improving compressive strength and durability (Li & Yu 2018).

7.1.2.3.1 SequestTech process

The challenge for commercial preparation of carbonated fly ash is to improve the rate of reaction to a useful level. In general, laboratory studies show that the carbonation reaction takes 2-4 hours to reach completion (e.g., Ukwattage et al. 2015), which is too slow for a bulk handling operation. In contrast to this, researchers at the University of Wyoming developed a fluidised bed carbonation process, called SequesTech, which effectively captured CO_2 within a few minutes (Reddy & Argyle 2011). A pilot plant was established at the Jim Bridges Power Plant in Wyoming, USA, where Class F fly ash (7.5 % CaO) was reacted with flue gas. The components of the SequesTech process are shown in Figure 43 below.

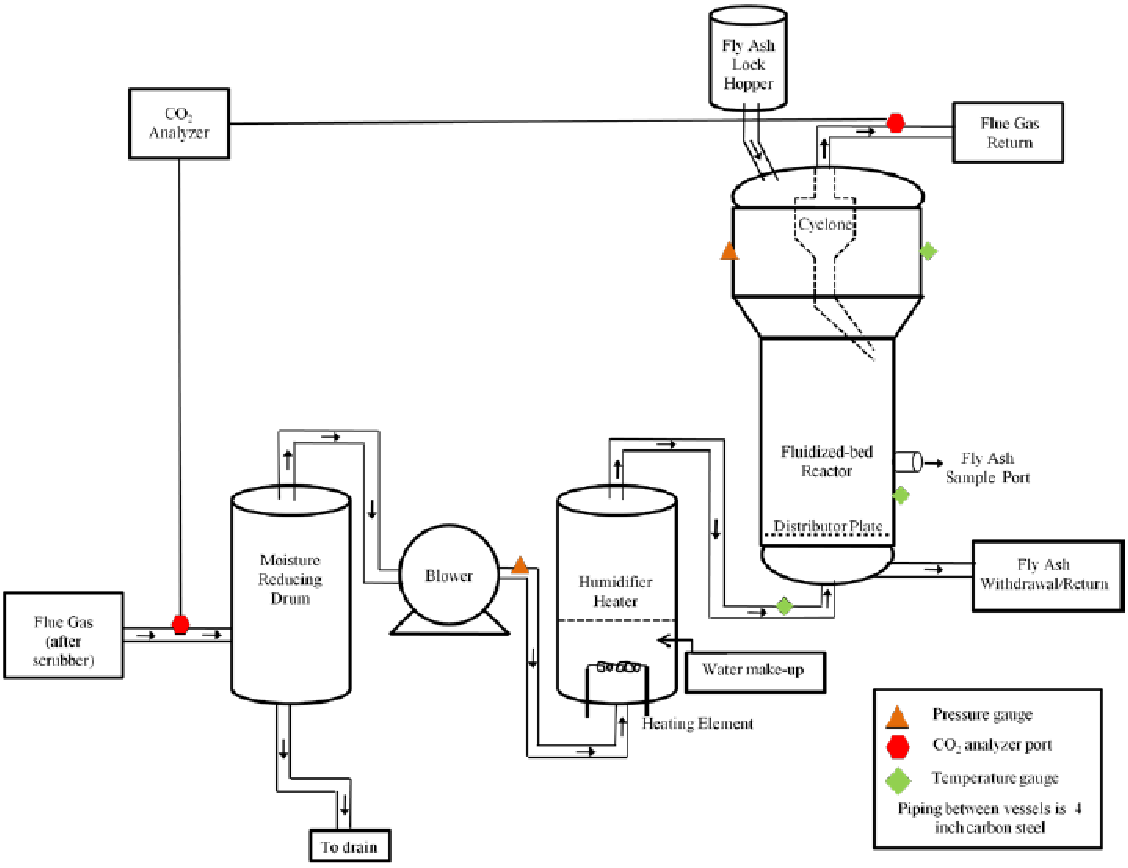

Figure 43: *SequesTech accelerated mineral carbonation concept (Reddy et al. 2010)*

Flue gas was withdrawn from the stack after the SO_2 scrubber and passed through a moisture reducing drum, a heater/humidifier and a fluidised bed reactor. The fluidised bed reactor was operated in batch mode with 100-300 kg fly ash, at a temperature of 35-90 °C. In this system, mineralisation was complete within a few minutes (Reddy et al. 2010). The process fixed about 207kg CO_2/tonne fly ash, and mineralised SO_2 and mercury from the flue gas (Reddy et al. 2011).

The SequesTech plant apparently operated over a period of seven years, removing 25-30 % of the CO_2 from 300-500 scfm of flue gas with a concentration of 11-12.5 % CO_2.[85] To date, however, this process has not yet been commercialised.[86]

Other researchers have shown that the carbonation reaction can be enhanced by adding wastewater or brine, particularly those with a pH over 9 and high concentration of bicarbonate/carbonate ions (Ji & Yu 2018). The carbonation reaction can also be enhanced by supplementing the fly ash with quicklime (CaO) or bubbling CO_2 through a slurry of quicklime in water (lime water) to create

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[85] https://cleantechnica.com/2011/05/11/ccs-pioneer-reddy-patents-new-co2-sequestration-tech/

[86] University of Wyoming, personal correspondence

microscopic particles of $CaCO_3$ prior to contact with fly ash (Qian et al. 2018). These strategies could be useful in boosting the amount of CO_2 captured by the fly ash, and for levelling out the differences between fly ashes from different sources.

7.1.2.3.2 Latrobe Magnesium process

In Victoria, Latrobe Magnesium uses carbonation as part of its proprietary process for extracting magnesium from lignite fly ash. In the first step of the process, a slurry of fly ash is reacted with strong alkali and CO_2, which drives the formation of $CaCO_3$ and maximises leaching of sulphur. Iron is removed using alkaline alkanolamine, then the remaining solids are filtered and calcined. Magnesium is then extracted using the Pidgeon thermal reduction process (Short 2013). The Latrobe Magnesium process converts waste lignite fly ash into valuable products, including magnesium metal, supplementary cementitious material (SCM), silica, char, iron oxide and calcium carbonate.

Latrobe Magnesium is constructing a 1,000 t/y demonstration magnesium production plant at Hazelwood North, originally scheduled for completion by the end of 2023.[87] In October 2023, it was announced that the project had been delayed by unforeseen external circumstances, so the company will initially focus on delivering the proprietary section of the process and produce magnesium oxide (MgO) as an initial commercial product. An agreement has been reached to sell the MgO to Rainstorm Dust Control, which utilises the product in its operations on both the eastern and western seaboards of Australia.[88]

7.1.2.4 Applications of carbonated fly ash

Carbonated fly ash may be regarded as a value-added product that not only sequesters CO_2 but can be used as a construction material. There are two ways by which carbonated fly ash could be monetised in the construction industry: (i) as a supplementary cementitious material, and (ii) as a carbonation-cured cement.

7.1.2.4.1 Fly ash as a supplementary cementitious material

The use of fly ash as a supplementary cementitious material in Portland cement concrete has many benefits and improves concrete performance. It improves the workability of wet concrete and increases the strength and durability of hardened concrete. It is cost effective, because it allows the amount of Portland cement to be reduced. Since the production of Portland cement is greenhouse gas intensive, the use of fly ash helps to reduce the environmental impact of cement production.[89]

Research has shown that using carbonated fly ash as a partial replacement for concrete results in improved resistance to salt, sulphate and acid solution. Consequently, carbonated fly ash has been recommended for use as a partial replacement for cement in concrete on the basis of its cost-effectiveness, ease of processing and greenhouse gas credentials (Sahoo et al. 2016).

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[87] https://smallcaps.com.au/latrobe-magnesium-demonstration-plant-start-up-in-early-2024

[88] https://smallcaps.com.au/latrobe-magnesium-accelerate-production-start-up-new-oxide-strategy/

[89] https://www.fhwa.dot.gov/pavement/recycling/fach03.cfm

7.1.2.4.2 Fly ash in carbonation-cured cement

High-calcium fly ashes will react and harden when mixed with water due to the formation of cementitious hydration products (Thomas 2007). If the calcium content of the fly ash is high enough, it is possible to make concrete with moderate strength using the fly ash as the sole cementing material (Cross et al. 2005). Under the right conditions, even low-calcium Class F fly ash can be reacted with CO_2 to produce solid cement. Researchers at the University of California 'shape stabilised' pastes of fly ash (both Class C and Class F) in moulds and then cured the pieces in a simulated water-saturated flue gas containing 12 % CO_2 at 75 ^{o}C for seven days. They demonstrated that cements made from either type of fly ash achieved a strength of around 35 MPa after seven days, with the strength gain proportional to the extent of CO_2 uptake (Wei et al. 2018). Hence, 'shape stabilised' pieces can be effectively carbonated simply by exposure to flue gas, making use of waste CO_2 and available heat to convert fly ash into useful construction materials (Wei et al. 2018).

7.1.2.5 Victorian Research Context

Victoria currently has three operational lignite-fired power stations in the Latrobe Valley. The total amount of fly ash produced in the Latrobe Valley is in the order of 500 kt/y, which is predominantly stored permanently in bunded retention ponds. Rather than being stored, this material could potentially be converted into low-emissions construction materials.

The only activity currently under way to add value to power station fly ash is the Latrobe Magnesium demonstration plant under construction at Hazelwood North. In the short term, this will produce MgO as an intermediate commercial product, but this will be upgraded to Mg metal when the full process is implemented. A cementitious additive material will also be produced from the Ca-rich residue.

7.1.2.6 ACI Comments

Class C fly ash is currently approved for use in concrete as a partial substitute for Portland cement. Victorian lignite fly ash is classed as neither Class C nor Class F, and variable in composition. However, the work by Cross et al. (2005), citied in Section 7.1.2.3.3.1.1 'Fly ash in carbonation-cured cement' above, showed that even Class F fly ash can make functional cement after carbonation.

This suggests that carbonation of fly ash with recycled CO_2 has the potential to convert a problematic waste into a new type of construction material. Carbonated fly ash has been recommended for use as a partial replacement for cement in concrete on the basis of its cost-effectiveness, ease of processing and greenhouse gas credentials (Sahoo et al. 2016).

It would be a relatively simple matter to upgrade lignite fly ash into a supplementary cementitious material, creating value from what is currently an intractable waste.

The SequesTech process demonstrated the carbonation of fly ash at TRL 6. In Victoria, the TRL is 4 for carbonation of lignite fly ash. Further R&D to develop this concept is strongly recommended.

The carbonation-granulation system developed by Carbon8 Systems has a TRL of 8 – 9. The potential of aggregated fly ash as a construction material produced in this manner is worthy of further consideration. ***Victoria should actively investigate the requirements to include carbonated fly ash in the concrete code for use in industry, ideally at Class C but even Class F.***

7.1.3 Early Carbonation Curing of Concrete and Cement

7.1.3.1 Current Status

Concrete is the most widely used construction material, consuming 2.6 billion tonnes per year of Portland cement and producing 1.88 billion tonnes of CO_2 emissions per year (Monteiro et al. 2013). Calcination of limestone for the production of cement produces about 5 % of global CO_2 emissions from all industrial processes and fossil-fuel combustion (Xi et al. 2016). The huge environmental significance of concrete use makes the development of ‘greener’ alternatives a high priority worldwide. The binding agent in concrete is Portland cement, which is a fine powder, produced by heating limestone and clay minerals in a kiln to form clinker, grinding the clinker, and adding 2 to 3 % of gypsum. When mixed with water, calcium silicates in Portland cement form hydration products which give the cement or concrete its strength (Zhang et al. 2017).

It has long been known that environmental exposure of concrete to CO_2 weakens its structure through decalcification of the calcium-silicate-hydrate. Counterintuitively, the idea of using CO_2 to accelerate the curing of Portland cement was proposed in the 1970s, but was not taken seriously because of concerns that the concrete would be weakened. Recently though, CO_2 curing has been seriously considered, and found to result in dramatically rapid strength gain, increased product resilience and improved durability, due to the altered composition and microstructure. This process is now known as ‘early carbonation curing’, to distinguish it from deleterious weathering carbonation (Zhang et al. 2017).

Early carbonation curing is regarded as a CO_2 sequestration process, since CO_2 is permanently stored in concrete in the form of calcium carbonate crystals. This has led to the development of a number of ‘green’ concrete production methods.

The initial approach was to use early carbonation curing as a conditioning step for masonry blocks and other moulded products, by exposure of freshly-demolded products in a chamber pressurised with CO_2 (e.g. El-Hassan et al. 2013; Shao et al 2014; Xuan et al. 2016). The general arrangement is shown in Figure 44 below.

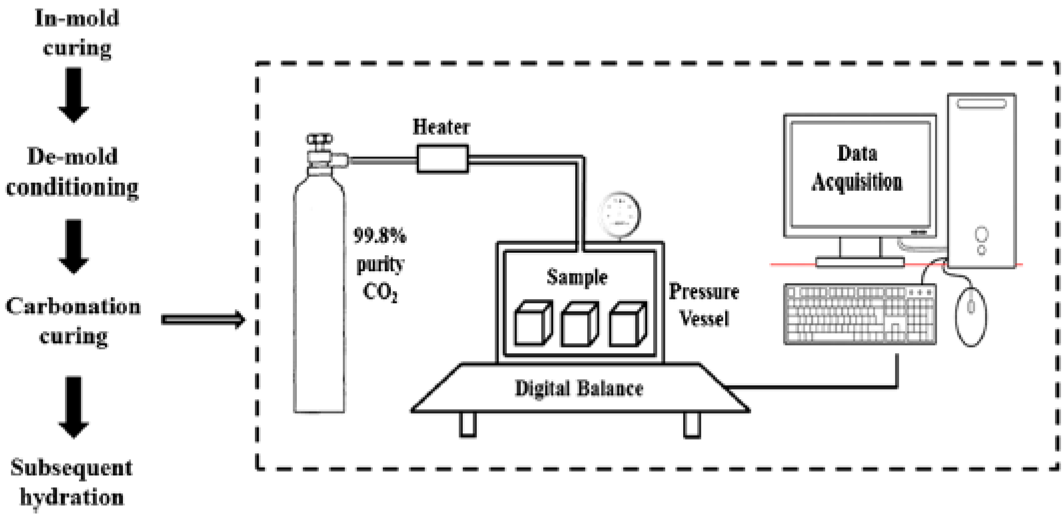

Figure 44: *Procedure of early carbonation curing (Zhang et al. 2016)*

This manufacturing procedure is restricted to manufacture of relatively small concrete items, and is limited by the capacity of the curing chamber and the time required for CO_2 to diffuse into the concrete products.

7.1.3.1.1 Solidia Technologies

Solidia Technologies, based in New Jersey USA, has developed a proprietary cement product, called Solidia Cement™, which requires CO_2 curing to set. Solidia Cement is made from similar ingredients as Portland cement, although in different proportions. The main difference between them is the way that they set and harden. Portland cement begins to cure as soon as it comes into contact with water and must stay moist throughout the entire process, which may take up to 28 days. Solidia Cement does not hydrate when exposed to water, and will not cure until it is simultaneously exposed to water and gaseous CO_2 (Sahu & DeCristofaro 2013).

Concrete products formed with Solidia Cement must be cured in an enclosed chamber pressurised with CO_2, as shown in Figure 30 above. The rate of curing is limited by the ability of gaseous CO_2 to diffuse throughout the part. Thin concrete products such as roof tiles (~10 mm thick) can be cured in less than 10 hours. Larger concrete parts, such as those in railroad sleepers (~250 mm thick), can be cured within a 24-hour period. As such, finished precast concrete products can be manufactured using Solidia Cement at a higher rate than with Portland cement (Sahu & DeCristofaro 2013).

In October 2022, Solidia announced a pivot from research to commercialisation, with relocation of its headquarters to a new 54,000-square-foot facility in San Antonio, Texas.[90]

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[90] https://apnews.com/press-release/business-wire/technology-texas-san-antonio-business-climate-and-environment-09eb0f1a1a1a4f16a6866f591523e8df

7.1.3.1.2 Carbicrete

Carbicrete, based at McGill University in Montreal, Canada, is developing a process that uses industrial waste to produce concrete products without the use of Portland cement (Shao et al. 2015). The process uses steelmaking ladle slag as a source of calcium and waste glass as a source of silica. These two materials are milled together in a defined proportion, compacted into cubic pallets and activated by heating, and then ground to a cementitious powder (Mahoutian et al. 2016). To make a concrete, the binder material is mixed with aggregate, e.g., steelmaking slag and water, and subjected to early carbonation curing in a CO_2 chamber. An example of a concrete block fabricated from steelmaking slag and glass is shown in Figure 45 below (Mahoutian & Shao 2016).

Figure 45: *Slag-glass concrete block (Mahoutian & Shao 2016)*

The novel concrete mix provides an environmentally friendly alternative to Portland cement, and can be used to fabricate a wide range of finished products (Shao & Mahoutian 2018).

The Carbicrete process has progressed from pilot scale to full commercial production and quality testing, with the first fully-cement free, carbon-negative concrete blocks available for sale in Canada in September 2023.[91]

7.1.3.1.3 CarbonBuilt

CarbonBuilt (formerly Carbon Upcycling), a start-up out of the University of California in Los Angeles, has developed a concept for a 'green' building material called CO_2NCRETE. The process starts with a calcium-rich waste material, such as steelmaking slag, which is leached and precipitated to produce solid portlandite ($Ca(OH)_2$). Prior to precipitation, or instead of, the Ca may be enriched using electro-osmotic dewatering[92]. The portlandite, along with leached slag granules, are combined with mineral aggregates, fly ash, water and rheology modifiers to produce a cementitious slurry suited for extrusion and shape stabilization. This is used to produce structural elements which are then cured in a pressurised chamber filled with CO_2, which is ideally sourced from flue gas. This converts the

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[91] https://carbicrete.com/carbicrete-cement-free-cmus-available/

[92] Lockhart, N. C. (1983). Electro-osmotic dewatering of fine tailings from mineral processing. *International journal of mineral processing*, *10*(2), 131-140.

portlandite to limestone (calcium carbonate), cementing the structure together (Wang et al. 2018) and sequestering CO_2 out of the atmosphere. The overall concept is illustrated in Figure 46 below.

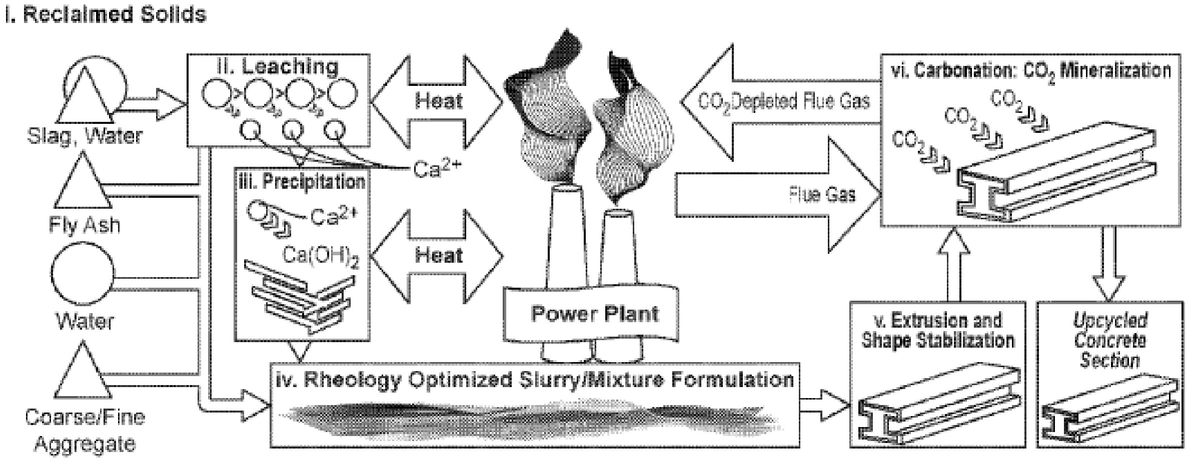

Figure 46: *Conceptual process for manufacturing CO_2NCRETE (Wang et al. 2018)*

In March 2023, CarbonBuilt signed a strategic partnership agreement with A3&Co®, a strategic and technical consulting firm, founded in the UAE and operating internationally, focusing on the cement sector. The partnership will support the engineering and project delivery of Carbon Upcycling's technology in the global cement and concrete industry.[93]

In May 2023, CarbonBuilt announced that commercial production of its low carbon concrete blocks had begun at Blair Block's concrete masonry production facility in Childersburg, Alabama.[94]

7.1.3.1.4 CarbonCure Technology, Inc.

For larger scale products, the Canadian company, CarbonCure Technology Inc. discovered that CO_2 can be directly injected into fresh concrete mixtures during mixing, making it possible to carbonate large batches of concrete prior to forming. CarbonCure has a portfolio of patents protecting its process (e.g. Forgeron et al. 2015; Forgeron et al. 2016; Niven et al. 2016), which essentially involve a metering system for injecting liquid CO_2 into concrete mix under controlled conditions. The liquid is converted into a mixture of CO_2 gas and CO_2 "snow" particles, which is injected into the fresh concrete prior to discharge into a truck. The injection metering system is contained in the box shown in Figure 47 below.

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[93] https://carbonupcycling.com/wp-content/uploads/2023/03/Joint-Press-Release_CarbonUpcycling_A3Co.pdf
[94] https://carbonbuilt.com/low-carbon-concrete-blocks-in-production/

Figure 47: *CarbonTech CO_2 injection system at a concrete batching plant*[95]

The amount of CO_2 actually incorporated into the concrete is actually quite small, about 2.3 kg of CO_2 in an 8 m^3 truck load. However, this amount is sufficient to increase the strength of the cement so that less is needed in the concrete, reducing the overall greenhouse gas emissions of the finished cement (Monkman et al. 2017). The mineralization of CO_2 is estimated to be greater than 80% of what is injected (Monkman 2018). CarbonCure is working to improve its greenhouse gas credentials further by using recycled CO_2 in its process. For example, the facility shown in Figure 47 uses CO_2 recovered from ethanol plant in Wisconsin. CarbonCure has also developed a measurement, reporting and verification (MRV) that tracks exactly how much CO_2 is injected into each amount of concrete, to support the tracing of carbon credits for its process.[96]

The performance of the CarbonCure process was validated by trials with a major user of the technology, who had used it at over 50 plants since 2016. Modified concrete mixture designs, with reduced Portland cement contents, were created to take advantage of the improved cement performance. The technology has been applied across more than 400 different mixtures including designs with varying binder compositions (e.g., neat cement, Type III cement, Portland limestone cement, ternary blends) and design strengths. The mix design adjustments achieved around a 7-8% reduction in the cement content without compromising the concrete strength or durability. The reduction of the cement in the concrete mixtures drives the environmental benefit, with a reduction of carbon intensity (kg CO_2/MPa) of 6 to 8%, or 22.8 to 29.2 tonnes CO_2 benefit per tonne of CO_2 used. The Chicago Department of Transportation (DOT) accepted the cement-reducing admixture in June 2019. More than 2.5 million m^3 of concrete have been shipped with an estimated net savings of 36,000 tonnes of CO_2 (Monkman et al. 2023).

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[95] https://concrete.ozinga.com/product/carboncure
[96] https://www.carboncure.com/carbon-removal/tracing-captured-co2-from-source-to-storage-in-concrete/

More than 650 CarbonCure systems have been sold in thirty countries, and its technologies have produced about 5 million truckloads of low-carbon concrete. It recently raised more than US$80 million in new equity to facilitate expansions in Europe, the Middle East, Latin America and Southeast Asia.[97] CarbonCure already has a presence in Australia, firstly through Canberra-based Hi-Quality Concrete[98], and more recently through a partnership with BOC.[99]

7.1.3.1.5 MIT precure carbonation

Researchers at the Massachusetts Institute of Technology (MIT) have recently reported that adding sodium bicarbonate (baking soda) to fresh concrete, while it is still at the slurry stage, can reduce the embodied carbon in the concrete by up to 15%. In addition to sequestering carbon, an advantage to adding baking soda is a faster-setting concrete mix that can allow formwork to be removed earlier, allowing for faster construction and completion of projects (Stefaniuk et al. 2023).

The manufacture of one tonne of cement causes about 0.87 tonnes of carbon dioxide emissions (global average). About half of the emissions from cement making are a result of heating limestone. When a cement rotary kiln reaches about 900°C the limestone ($CaCO_3$) decomposes into lime (CaO), and releases CO_2 as a waste product. The other half of the emissions associated with cement production are through combustion of fuels to produce heat for the rotary kiln and to generate the electricity used to grind and transport material. Globally, the manufacture of cement produces more greenhouse gas emissions than any other single product – about 3 billion tonnes per year, or 8% of the world total (Beyond Zero Emissions 2017).

The MIT researchers found that by substituting 20% baking soda into the concrete formulation, about 30% cement was required, reducing the overall total CO_2 emissions from concrete production by 15%. They estimated that an emissions reduction of as much as 20% should be theoretically possible, although more work is needed (Stefaniuk et al. 2023).

The resulting concrete sets much more quickly via the formation of a previously undescribed composite phase, a mix of calcium carbonate and calcium silicon hydrate (C-S-H), as shown in Figure 48 below. This is a completely new development that can double the mechanical performance of the early-stage concrete without impacting its mechanical performance.[100]

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[97] https://carboncredits.com/carboncure-carbon-removal-technologies-for-conrete-raises-over-8m/

[98] https://www.hqconcrete.com.au/carboncure

[99] https://www.boc-gas.com.au/en/industries/construction_infrastructure/concrete/index.html

[100] https://energypost.eu/adding-ordinary-baking-soda-to-concrete-production-can-cut-15-of-its-co2-emissions/

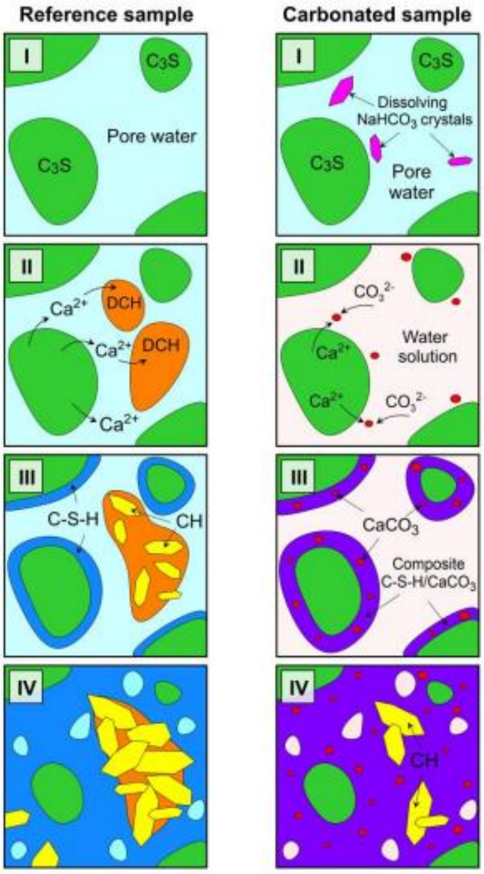

Figure 48: *Early-stage hydration reactions (precure I-III and postcure IV) for samples with and without bicarbonate substitution. CH: calcium hydroxide (portlandite). DCH: disordered CH (Stefaniuk et al. 2023)*

7.1.3.2 Victorian Research Context

ACI is unaware of any commercial or research activity in the area of early carbonation curing in Victoria.

7.1.3.3 ACI Comments

The processes being developed by Solidia, Carbicrete and Carbon Upcycling UCLA are all dependent on the availability of a high-Ca feedstock, such as blast furnace slag. In a similar manner, it is possible that lignite fly ash may be suitable for fabricating new construction materials using early carbonation curing, but this is mere speculation at this stage. Given the labour-intensity of curing formed pieces in a carbonation chamber, and the uncertainty about the performance of such materials, this is not considered to be a high priority for research.

Conversely, ***the process of direct injection of CO_2 into fresh concrete, under development by CarbonCure Technology, is technically viable and a proven way to reduce the CO_2 footprint of concrete products. CarbonCure has recently partnered with BOC to facilitate deployment of the technology in Australia. As such, this is a technology that can be adopted immediately.***

The CarbonCure process reduces the amount of Portland cement needed in a concrete mixture by 7-8%. This is only a quarter of the reduction achieved by MIT researchers by adding baking soda to the *batch. Given that baking soda is easily produced by reacting CO_2 with sodium hydroxide (see Section 7.4 below), and does not require any specialised equipment, this represents an exciting opportunity to permanently sequester significant quantities of captured CO_2.* ***ACI recommends that the potential for addition of baking soda during concrete production should be a high priority for research in Victoria.***

7.2 PRECIPITATED CALCIUM CARBONATE

7.2.1 Current Status

Calcium carbonate ($CaCO_3$) is one of the most abundantly occurring minerals, existing naturally in the form of limestone, marble and chalk. For industrial applications, two main forms of calcium carbonate are used: fine ground calcium carbonate and precipitated calcium carbonate (PCC). They are both used as fillers in plastics, paints, concrete and composite materials, and as pigments, processing aids and extenders. The global calcium carbonate market size was valued at US$20.69 billion in 2016 and is expected to be valued at US$34.28 billion by 2025 (Grand View Research 2018).

Although the two product types have similar applications, PCC is composed of relatively smaller sized particles, is relatively brighter and also has relatively higher calcium carbonate content as compared to fine ground calcium carbonate. It is considered a premium product, being a refined form of limestone, and represents about 19% of the total calcium carbonate market (Teir et al. 2016).

PCC is produced from lime, which is manufactured by calcining limestone ($CaCO_3$) in a kiln at temperatures over 900^oC:

$$CaCO_3 \rightarrow CaO + CO_2$$

The lime (calcium oxide) is hydrated with water into a calcium hydroxide slurry:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

CO_2 is injected into the slurry, where it reacts with calcium hydroxide to form calcium carbonate, which precipitates out:

$$Ca(OH)_2(aq) + CO_2 \rightarrow CaCO_3(s) + H_2O$$

This process removes impurities from the limestone, and the resulting PCC is extremely white and typically has a uniform narrow particle size distribution. By adjusting the precipitation process parameters, the shape and size of the crystals produced can be controlled to optimize their optical properties. The two main crystal morphologies desirable for papermaking are shown in Figure 49 below.

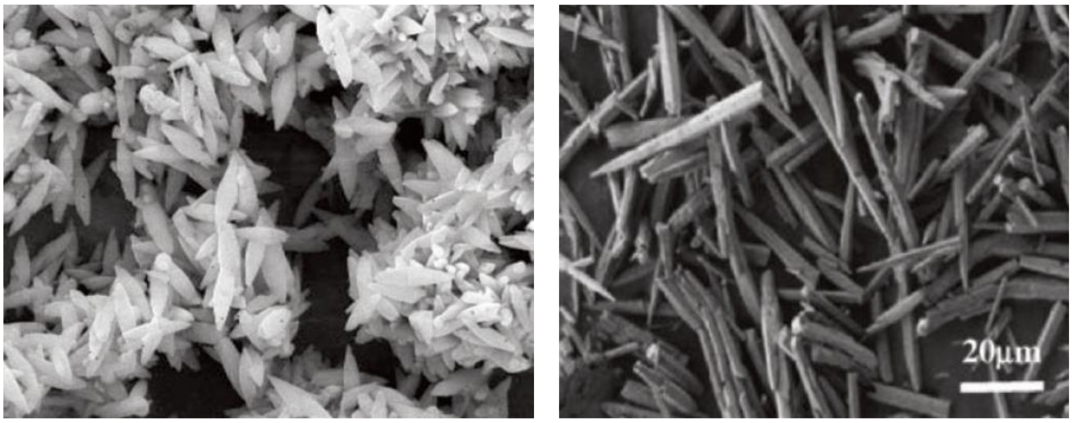

Figure 49: *Forms of $CaCO_3$ used in the paper industry: (a) scalenohedral calcite, (b) aragonite*[101]

PCC is the preferred product for use in papermaking, where it results in better printing surfaces and brighter papers, improves paper machine productivity, and can reduce papermaking costs through the replacement of more expensive pulp fibre. PCC is typically produced in slurry form at satellite plants located near paper mills. PCC is also used in paints, plastics and sealants, as well as in healthcare, for formulation of high dosage calcium supplements and calcium fortified foods and beverages.[102]

Note that PCC has the same chemical composition as the parent limestone, minus the impurities. Even though CO_2 is bound during the PCC production process, a larger amount of CO_2 is released during the lime production, due to the fuel burned to provide heat for the calcination reaction. Consequently, production of PCC from limestone is a net emitter of greenhouse gases, with a global warming potential (GWP) of 1.0 t $CO_{2\text{-eq}}$/t PCC (Teir et al. 2016). With the anticipated rising demand for PCC, there is a need to develop a more environmentally friendly production route with less greenhouse gas emissions.

A step toward an alternative method for PCC production was made by researchers at the University of Tokyo, in the course of research on indirect mineral carbonation for CO_2 sequestration. Their concept was to use acetic acid to extract calcium ions from calcium metasilicate ($CaSiO_3$) minerals (Kakizawa et al. 2001). Despite promising early results, the research was discontinued because the process was not economical for CO_2 capture and storage.

7.2.1.1 Slag2PCC process

This concept was taken up by researchers in Finland, during the development of a process called Slag2PCC, in which PCC was produced from steelmaking slag. This was a collaborative project involving Finnish industry and research organisations that ran between 2011 and 2016. Preliminary experiments verified that acetic acid was efficient for dissolving steelmaking slags, but precipitation of calcium carbonate from the resulting solution required the addition of NaOH, adding to the process

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[101] Aalto University School of Engineering, “Success story on mineral carbonation of CO_2”, www.energytech.aalto.fi/en

[102] https://www.lime.org/lime-basics/uses-of-lime/other-uses-of-lime/precipitated-calcium-carbonate/

cost (Teir et al. 2007). It was subsequently found that ammonium salt solutions (e.g. chloride, nitrate or acetate) could dissolve steelmaking slag and be recycled for reuse after precipitation (Elenova et al. 2009). The process was patented (Teir et al. 2009) and developed further during the Slag2PCC project.

The chemical reactions of the Slag2PCC technology are shown below.

$$CaO_{(s)} + 2NH_4X_{(aq)} + H_2O_{(l)} \rightleftharpoons CaX_{2(aq)} + 2NH_4OH_{(aq)}$$

$$2NH_4OH_{(aq)} + CO_{2(g)} \rightleftharpoons (NH_4)_2CO_{3(aq)} + H_2O_{(l)}$$

$$(NH_4)_2CO_{3(aq)} + CaX_{2(aq)} \rightleftharpoons CaCO_{3(s)} + 2NH_4X_{(aq)}$$

Where CaO represents all ammonium salt soluble calcium regardless of the actual crystal form in which it is bound. The salt, X, can be chloride, nitrate or acetate (Mattila et al., 2014). The basic flow diagram for this process concept is shown in Figure 50 below.

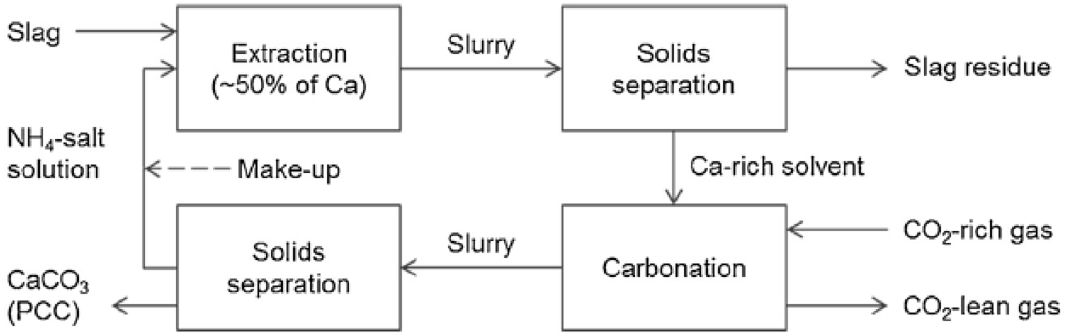

Figure 50: *Conceptual flow diagram of the Slag2PCC process (Teir et al. 2016)*

After extraction, the calcium salt solution is separated from the slag residue by filtration and passed to the carbonation reactor, where calcium carbonate is precipitated by bubbling CO_2 through the solution. This process regenerates the ammonium salt, which can be separated by filtration and recycled to the extraction vessel.

To develop this process, a 30 litre bench-scale unit was first built and tested in Åbo Akademi University, after which a 200 litre pilot facility was constructed and tested in Aalto University. The various process steps were both experimentally tested and mathematically modelled, and a conceptual design for a demonstration plant was developed. A techno-economic assessment showed that the process could be economically viable. The overall global warming potential (GWP) of the process was estimated to be -0.3 t $CO_{2\text{-eq}}$/t PCC, making it much more environmentally friendly than production of PCC from limestone (Teir et al. 2016).

The Slag2PCC technology does not seem to have progressed beyond pilot scale. It is perhaps significant that this process is essentially the same as that patented by Blue Planet (see Section 7.1.1.2), so IP considerations may have hindered commercialisation efforts.

7.2.1.2 Carbon Engineering process

Canadian company, Carbon Engineering, one of the leading proponents of direct air capture (DAC), uses the standard quicklime-based CO_2-to-PCC reaction (Section 7.2.1) to absorb CO_2 from ambient air. The resulting slurry of amorphous calcium carbonate is recirculated through a crystallization reactor to produce mechanically stable calcium carbonate crystals (Heidel et al. 2023). The crystals are then sent to a calciner, where heat is applied to dissociate CO_2 and regenerate CaO for reuse (Sodiq et al. 2023), as shown in Figure 51 below.

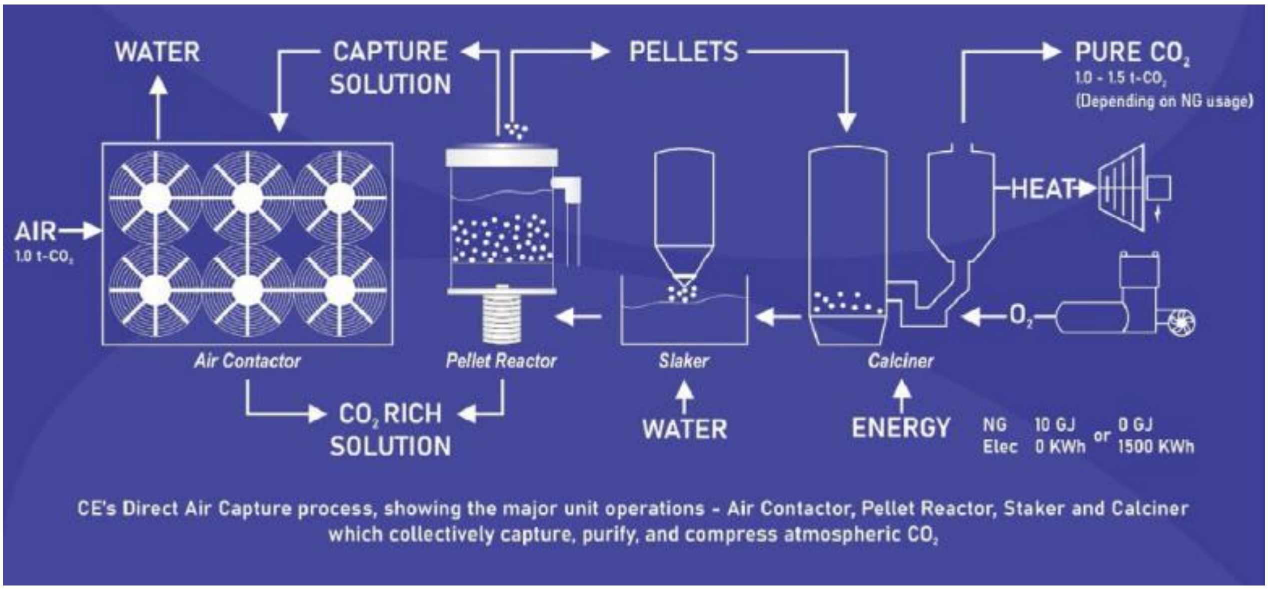

Figure 51: *Carbon Engineering process for direct air capture via calcium carbonate (Sodiq et al. 2023)*

7.2.2 Victorian Research Context

Researchers at Monash University and CSIRO in Melbourne have developed a process similar to Slag2PCC for extracting calcium carbonate and/or magnesium carbonate from the fly ash produced at lignite-fired power stations in the Latrobe Valley. As in the Slag2PCC process, the proposed fly ash carbonation process using ammonia chloride as a regenerative solvent. The concept for this process is illustrated in Figure 52 below.

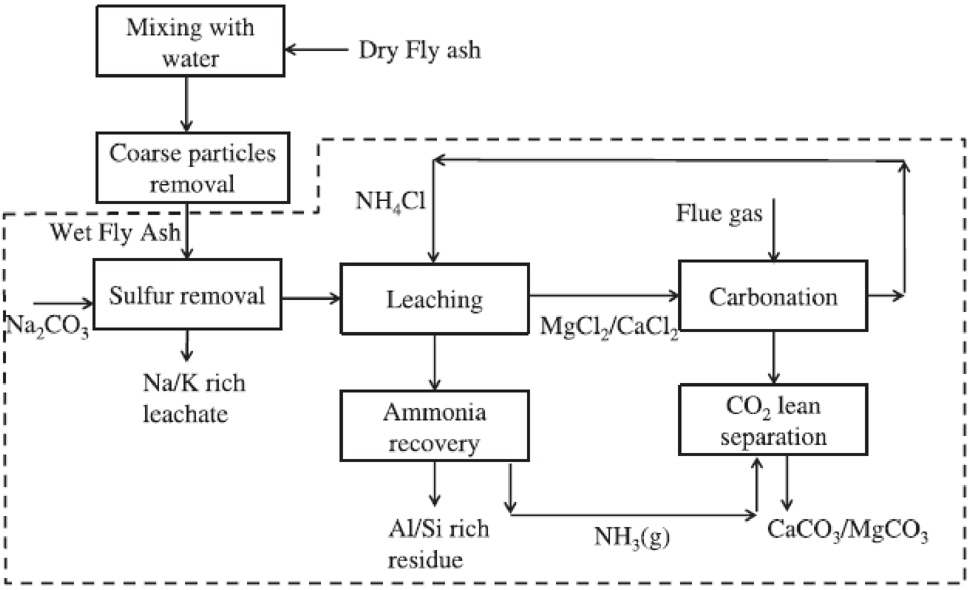

Figure 52: *Block flow diagram for carbonation of lignite fly ash (Hosseini et al. 2016)*

This process was originally conceived as a mineral carbonation process for CO_2 sequestration, however, a techno-economic assessment found that it was too expensive to be viable in this application (Hosseini et al. 2016). The fly ash from Victorian power stations contains both calcium and magnesium, so the process allows for the production of both calcium carbonate and magnesium carbonate, which can be treated as value-added products.

It was found that fly ash from the Hazelwood power station produced a mixture of magnesium carbonate and calcium carbonate in varying proportions with less than 8 % impurities, which is a similar composition to dolomite. Dolomite (calcium magnesium carbonate $CaMg(CO_3)_2$) is used as a source of magnesium in agriculture, and is also used in steelmaking. However, these are relatively low value applications (Hosseini et al. 2016).

7.2.3 ACI Comments

The Monash University results indicate that magnesium and calcium carbonates will form simultaneously if both species are present in the system. This represents a significant limitation of using this approach for producing pure precipitated calcium carbonate, and possibly applies to the Slag2PCC process as well.

However, the precipitates formed in the Monash University process could also be formed into aggregates for use in the construction industry, in which case it would be essentially the same as the Blue Planet process (Section 7.1.1.2). Blue Planet is actively developing its aggregate as a carbon-negative construction material for permanent CO_2 sequestration, and is attracting significant interest from industrial partners. Blue Planet does not appear to have patented its process in Australia, and Monash University has not continued its research in this area.

There would appear to be an opportunity for local development of the Monash University / Blue Planet mineralisation process, to add value to the vast stockpile of fly ash in the Latrobe Valley through CO_2 *sequestration.*

The Carbon Engineering process produces pure calcium carbonate as an internal product, before calcining it to displace CO_2 *and recover CaO for recycle. This is only possible because pure limestone is used as the source of calcium, effectively replicating the conventional process for manufacture of PCC calcium carbonate. As such, it does not represent a new development.*

7.3 PRECIPITATED MAGNESIUM CARBONATE

7.3.1 Current Status

The sequestration of CO_2 by precipitating it with magnesium ions to form nesquehonite ($MgCO_3 \cdot 3H_2O$) was proposed by Ferrini et al. (2009). The advantages of this process for carbon capture were stated as:

a) the process is kinetically favored and simple

b) nesquehonite formation occurs in a very short time

c) it is a thermodynamically and chemically stable solid product, allowing for long-term storage of CO_2

d) the starting reactants were locally abundant

e) nesquehonite can potentially be used for industrial purposes, and its disposal near the surface or underground involves limited environmental risks

Ferrini et al. (2009) suggested that suitable sources of magnesium ions would be seawater or rejected brine from desalination plants.

7.3.1.1 Carbon Capture Machine

Carbon Capture Machine (CCM), based at the University of Aberdeen in Scotland, is developing technology for production of high purity carbonate minerals with applications in construction, paper and other industries.

In CCM's proprietary process, captured CO_2 is dissolved in dilute alkali, then reacted with calcium- and/or magnesium-rich brine to selectively precipitate calcium carbonate and magnesium carbonate (Imbabi et al. 2016; Imbabi et al. 2017). Since Calera Corporation has developed a patent portfolio around production and applications of precipitated calcium carbonate, CCM is focusing its efforts on magnesium carbonate.

Laboratory trials have shown that, under alkaline conditions, Mg ions precipitate as nesquehonite, $MgCO_3.3H_2O$, in the form of hexagonal needles, as shown in Figure 53 below. The dried needles are easily disaggregated to form a flowing powder (Morrison et al. 2016).

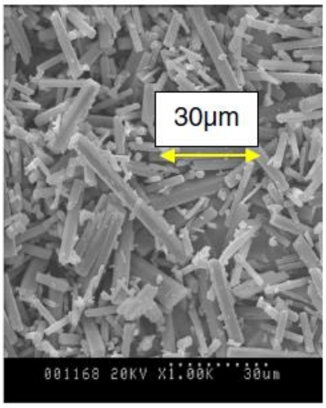

Figure 53: *Precipitated needles of magnesium carbonate (Morrison et al. 2016)*

Nesquehonite can be activated by gentle heating in air. Remarkably, almost all water can be removed while the crystal morphology remains largely intact. The activation temperature is kept below 275 °C to ensure that no loss of CO_2 occurs. The activated precursor is then mixed with water to form a slurry which can be cast in moulds and harden. After 24 hours the cast items develop a compressive strength of 7-12 MPa, comparable with commercial gypsum board. The hardened product is porous and has a low bulk density in the range 700–850 kg/m^3. Samples have been left in the laboratory atmosphere at room temperature for approximately six months and remained essentially unchanged (Morrison et al. 2016).

CCM is developing a lightweight, insulating plasterboard based on precipitated magnesium carbonate. The product is reported to be water resistant, non-toxic, fire-proof, with superior thermal and acoustic insulation properties, and the ability to be cut and fastened using conventional methods. Future applications in cement and concrete are under development.[103]

This process is still in the early stages of development, and has not progressed beyond the lab pilot scale.

7.3.2 Victorian Research Context

As mentioned in Section 7.2.2 above, the team led by Professor Lian Zhang at Monash University has developed a proprietary process which allows the selective fractionation of the calcium carbonate and magnesium carbonate products from lignite fly ash. These researchers sought support from local industry for developing a magnesium carbonate plasterboard product to replace imported product, without success.

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[103] https://ccmuk.com/technology

As discussed in Section 7.1.2.3.2 above, Latrobe Magnesium is planning to produce MgO from fly ash in the first stage of implementing its magnesium recovery process at demonstration scale. The MgO, which will also contain a substantial proportion of CaO, will be sold for use in dust control.

7.3.3 ACI Comments

Magnesium carbonate construction boards are already available in the Australian market, fabricated from minerals mined overseas. To date there has been insufficient support from local industry to develop an alternative, but this may change if a green product embodying captured CO_2 can offer a market advantage. A modification of the Monash University / Blue Planet mineralisation process could be used to produce both magnesium carbonate and calcium carbonate. ***ACI recommends that the Monash University process should be further developed to pilot scale (TRL 6), so that samples can be produced for product development and market evaluation.***

7.4 SODIUM CARBONATE AND SODIUM BICARBONATE

7.4.1 Current Status

Sodium carbonate, Na_2CO_3, also known as soda ash, is a major commodity and an essential raw material for many industrial applications. It is mainly used in the manufacture of glass and in the production of chemicals (e.g. sodium silicates and sodium phosphate). It is also used in processing wood pulp to make paper, in making soaps and detergents, in refining aluminium, in water softening, etc. In nature, it is found in arid regions as extensive beds of sodium minerals and as sodium-rich waters (brines) (Thieme 2000).

Sodium bicarbonate, $NaHCO_3$, also known as bicarb soda or baking soda, is used mainly in production of animal fodder (as an acidity regulator), food (as an ingredient of baking powder and sparkling drinks), pharmaceuticals, detergents and cosmetics, and for purifying exhaust fumes (mainly for desulphurisation). In the chemical industry it is used for production of pigments and explosives as well as a basic component of fire extinguishers. The baking soda market is divided into the segments of low, high and very high-quality baking soda. The high-quality segment covers food and pharmaceutical industries. Very high quality is required for medical purposes — e.g., in hemodialysis (Thieme 2000).

Sodium bicarbonate is produced industrially from sodium carbonate:

$$Na_2CO_3 + CO_2 + H_2O \rightarrow 2\ NaHCO_3$$

In 2022, global production of soda ash was 63.37 million tonnes. Production is forecast to increase to around 74.07 million tonnes by 2030.[104] The value of the soda ash market was US$18.25 billion in

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[104] https://www.statista.com/statistics/1245254/soda-ash-market-volume-worldwide/

2022 and is forecast to grow to US$24.01 billion by 2030, a compound annual growth rate of 4.00%.[105]

Global production of sodium bicarbonate is currently about 7.2 million tonnes per year,[106] with a value of US$1.4 billion in 2022. This value of this market is forecast to grow to US$2.2 billion by 2030.[107]

In Wyoming, USA, large deposits of the mineral trona, $Na_3HCO_3CO_3{\cdot}2H_2O$, are mined as an inexpensive domestic source. In countries where there are no economically mineable local resources, sodium carbonate is predominantly manufactured by the Solvay ("ammonia-soda") process. Up until 2014, sodium carbonate was manufactured in Australia by Penrice Soda Products at Osborne, SA using the Solvay process. Penrice produced sodium carbonate for 80 years at Osbourne, using a natural brine and limestone as raw materials. It was shut down in 2014 due to poor financial performance. At that time it was the fifth largest producer in the world.[108] Australia now relies on imported supplies of sodium carbonate and sodium bicarbonate.

7.4.1.1 Solvay process

The Solvay process involves 6 distinct chemical reaction steps, with CO_2 being an important chemical input. The CO_2 is produced by the calcination of limestone to CaO and CO_2:

$$CaCO_3 \rightarrow CaO + CO_2$$

The CO_2 is used to carbonate ammonia (NH_3), which is dissolved in a saturated NaCl brine, producing sodium bicarbonate ($NaHCO_3$) and ammonium chloride (NH_4Cl):

$$2NH_3 + 2CO_2 + 2H_2O \rightleftharpoons 2NH_4HCO_3$$

$$2NH_4HCO_3 + 2NaCl \rightleftharpoons 2NaHCO_3 + 2NH_4Cl$$

The sodium bicarbonate is decomposed by heating to produce sodium carbonate, releasing CO_2:

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$$

The calcium oxide, produced from limestone, is mixed with water to form 'milk of lime' a suspension of calcium hydroxide, which is used for the recovery of ammonia:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

$$2NH_4Cl + Ca(OH)_2 \rightleftharpoons 2NH_3 + CaCl_2 + 2H_2O$$

The overall reaction for the Solvay process is:

$$2NaCl + Ca(OH)_2 \rightleftharpoons 2NH_3 + CaCl_2 + 2H_2O$$

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[105] https://www.marketresearchfuture.com/reports/soda-ash-market-2339
[106] https://ciechgroup.com/en/relacje-inwestorskie/market-environment/soda-segment/sodium-bicarbonate/
[107] https://www.researchandmarkets.com/report/baking-soda
[108] https://autopsyofadelaide.com/2017/01/05/urban-exploration-the-penrice-soda-factory/

Even though the Solvay process uses CO_2 as a reaction input, it is released again during the decomposition of sodium bicarbonate to carbonate, and can be recycled. The high energy requirement for calcining limestone means that the Solvay process is a net emitter of CO_2, producing 0.2-0.4 t CO_2/t Na_2CO_3 (Steinhauser 2008).

The Solvay process also produces a large quantity of limestone residue and calcium chloride, which are often disposed of by pumping out to sea (Steinhauser 2008). These environmental concerns have prompted research efforts to develop more environmentally friendly ways to produce sodium carbonate. These have been reviewed elsewhere (Quang et al. 2019) and will not be discussed here.

7.4.1.2 EnPro AS

A more environmentally friendly modification of the Solvay process has been developed by EnPro AS, of Norway. EnPro's process involves production of sodium carbonate and sodium bicarbonate using CO_2 from industrial flue gas.

In EnPro's process, CO_2 is reacted with quicklime $Ca(OH)_2$ to produce a clear solution of calcium bicarbonate $Ca(HCO_3)_2$:

$$Ca(OH)_2 + 2\ CO_2 \rightleftharpoons Ca(HCO_3)_2$$

Calcium bicarbonate (500 to 1000 ppm) is then processed by a cation exchange system to produce sodium bicarbonate $NaHCO_3$ (500 to 1000 ppm):

$$Ca(HCO_3)_2 + 2\ R - Na^+ \rightleftharpoons 2\ NaHCO_3 + R - Ca^{2+}$$

The availability of brine water with a salinity of 8 to 12% is crucial to EnPro's process because it is used to regenerate the cation exchanger:

$$R - Ca^{2+} + 2NaCl \rightleftharpoons 2R - Na^+ + CaCl_2$$

The sodium bicarbonate liquor produced is of low percentage, i.e., 0.05 to 0.1 %, and needs to be concentrated. The concentration is performed using reverse osmosis, in which the bicarb soda liquor is taken through multiple passes until the final concentrate output is around 6 %. EnPro relies on the use of industrial waste heat to create high efficiency in $NaHCO_3$, Na_2CO_3, and NaOH production (Engsl & Farhat 2014)

The Enpro process is being investigated at pilot scale by Enpro's technology partner, ENGSL Minerals DMCC in the UAE.[109]

Note that the reaction of CO_2 with quicklime in the Enpro process is the same reaction used for production of precipitated calcium carbonate (Section 6.3.1) and Carbon Engineering's DAC process (Section 6.3.1.2). By passing the reaction mixture over an ion exchange column, Enpro drives the equilibrium away from insoluble $CaCO_3$ and toward soluble $NaHCO_3$.

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[109] http://www.gdccus.org/en/nd.jsp?id=197

Also note that, by analogy with Carbon Engineering, the Enpro process could be used as the basis of a DAC system.

7.4.1.3 Skyonic Corporation / CarbonFree

Skyonic Corporation, of Austin, Texas, has developed a process similar to that of New Sky Energy, which it calls SkyMine®, using a conventional chlor-alkali electrolysis system (Jones & St. Angelo 2015). The principle of the chlor-alkali cell is shown in Figure 54 below.

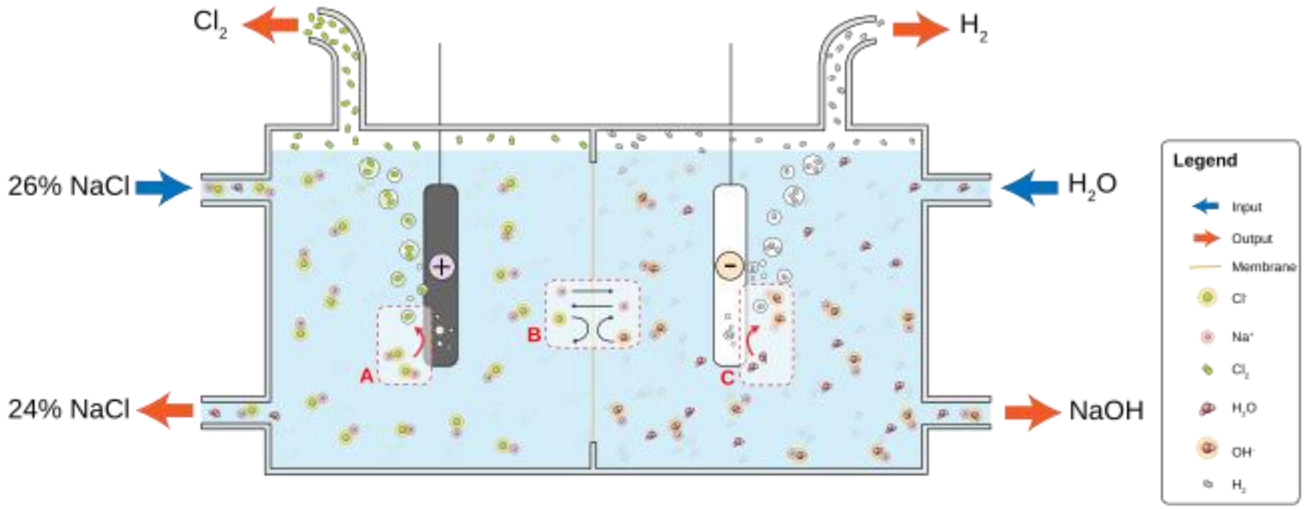

***Figure 54:** Basic membrane cell used in chlor-alkali electrolysis of brine*[110]

The inputs to the chlor-alkali process are salt (NaCl), water and electricity. Saturated brine is passed into the first chamber of the cell where the chloride ions (Cl^-) are oxidised at the anode (A), losing electrons to become chlorine gas (Cl_2).

$$2\,Cl^- \rightarrow Cl_2 + 2e^-$$

The ion-selective membrane (B) allows the counterion Na^+ to freely flow across, but prevents anions such as hydroxide (OH^-) and Cl^- from diffusing across. At the cathode (C), water is reduced to OH^- and hydrogen gas.

$$2\,H_2O + 2e^- \rightarrow H_2 + 2\,OH^-$$

Sodium ions (Na^+) pass through the ion-selective membrane to the second chamber, where they react with the hydroxide ions to produce sodium hydroxide (NaOH). The overall reaction for the electrolysis of brine is thus:

$$2\,NaCl + 2\,H_2O \rightarrow Cl_2 + H_2 + 2\,NaOH$$

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[110] https://en.wikipedia.org/wiki/Chloralkali_process

The chlor-alkali process thus uses electricity to convert an aqueous solution of NaCl into the industrially useful products, sodium hydroxide (soda ash) and chlorine gas.

The SkyMine® process makes use of the generated chlorine and hydrogen to produce hydrochloric acid (HCl) and sodium hypochlorite (NaClO) bleach solution. Sodium hydroxide is used capture CO_2 from industrial flue gas, producing sodium bicarbonate (baking soda), as shown in Figure 55 below.

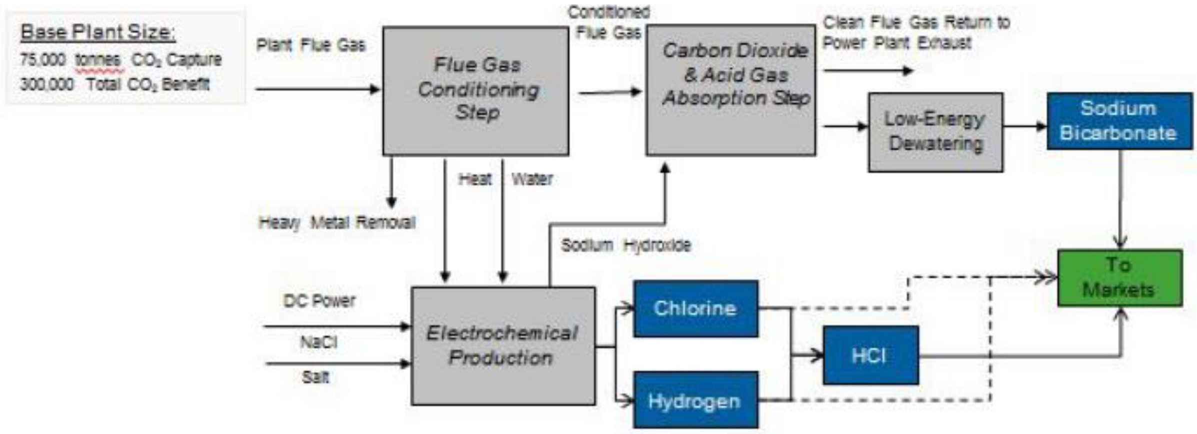

Figure 55: *Skyonic Corporation's SkyMine™ process (Walters 2016)*

In 2010, Skyonic received US$25 million from the U.S. Department of Energy to support construction of a commercial-scale SkyMine® plant adjacent to the Capitol Aggregates cement plant in San Antonio, Texas. Commissioned in 2016, the SkyMine® plant captures 50,000 t/y CO_2 from the cement plant flue gas for mineralisation. The plant produces sodium bicarbonate ($NaHCO_3$), hydrochloric acid (HCl), sodium hydroxide (NaOH), and sodium hypochlorite (NaClO), and operates as a stand-alone profitable business.

In 2016, Skyonic Corporation was aquired by CarbonFree Chemicals. The combined organisation, known as CarbonFree, does not intend to scale up the SkyMine® process but is instead focussing on a second-generation technology called SkyCycle®. The reason for this is that sodium bicarbonate does not provide a long-term sequestration option for CO_2, and is a relatively small market. SkyCycle® will produce precipitated calcium carbonate, or PCC, which can store carbon for centuries or millennia.[111] The SkyCycle® process is a form of mineral carbonation, producing produce $CaCO_3$ or $MgCO_3$ from inosilicate minerals such as $CaSiO_3$ (wollastonite), $MgSiO_3$ (enstatite), and $MgO.FeO.SiO_2$ (e.g., olivine, pyroxine) (Jones & Yablonsky 2016). This process has been proven at pilot scale, and opportunities for commercialisation are being sought. However, the inosilicate minerals suited to this process are not present in Victoria in significant quantities (McHaffie & Buckley 1995).

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[111] https://carbonfree.cc/carbonfree-is-already-a-profitable-carbon-capture-business-ceo-martin-keighley/

7.4.1.4 New Sky Energy

New Sky Energy, formed in 2007 in Boulder CO, has developed three unique technologies: SulfurSolve®, SaltCycle®, and CarbonCycle®, and services customers in the oil and gas, mining and minerals, and water treatment industries. SulfurSolve is used to remove hydrogen sulphide (H_2S) from gas streams, particularly for sweetening biogas. SaltCycle is used to selectively recovers useful industrial salts (e.g., sodium sulphate) from waste brine streams, and has proved useful in the fabric dying industry.

CarbonCycle is an electrochemical process that captures and converts CO_2 into sodium carbonate or soda bicarbonate. The heart of a process is a membrane-based water electrolysis unit, which uses renewable energy to create separate streams of acid and alkali, plus hydrogen as a by-product. The alkali stream is used to capture CO_2 and convert it into sodium carbonate salts (Little et al. 2012).

The mechanism of reaction between CO_2 and the alkali depends on the concentration of the alkali solution. When the alkali (NaOH) solution is very dilute (pH 8-9), carbon dioxide will first react with water to form carbonic acid (H_2CO_3) slowly. The acid thus formed then reacts with the alkali to give sodium bicarbonate ($NaHCO_3$).

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

$$NaOH + H_2CO_3 \rightleftharpoons NaHCO_3 + H_2O$$

When the alkali solution is fairly concentrated (pH>11), it reacts directly with CO_2 to form the bicarbonate, which further reacts with NaOH to form sodium carbonate (Na_2CO_3).

$$NaOH + CO_2 \rightleftharpoons NaHCO_3$$

$$NaHCO_3 + NaOH \rightleftharpoons Na_2CO_3 + H_2O$$

If required, soluble sodium carbonate can be reacted with $CaCl_2$ or $MgCl_2$ to form $CaCO_3$ or $MgCO_3$ as insoluble products.

In contrast to the chlor-alkali process used in the SkyMine® process, which produces NaOH and Cl_2 gas from NaCl electrolyte, the CarbonCycle process produces NaOH and sulphuric acid (H_2SO_4) from sodium sulphate (Na_2SO_4) electrolyte (Little et al. 2012). This is accomplished using bipolar membrane electrodialysis (EDBM), which is a commercial technology used in the water treatment industry. EDBM combines electrodialysis for salt separation with electrodialysis water splitting, resulting in conversion of a salt into its corresponding acid and base, as shown in Figure 56 below.

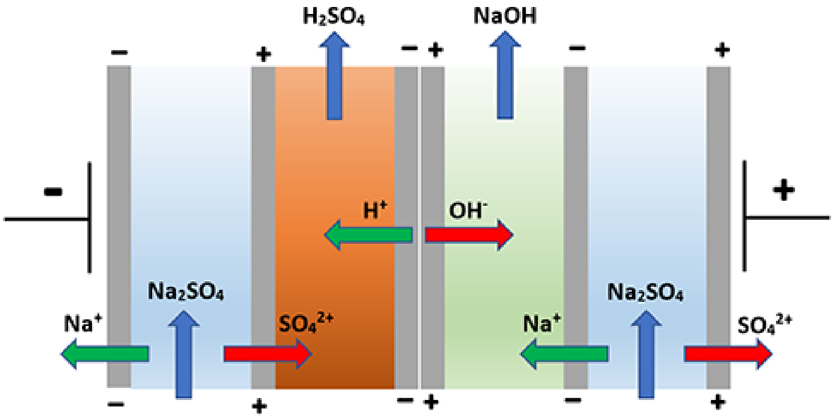

Figure 56: *Schematic process of splitting salts to their corresponding acids and bases by EPDM* [112]

EPDM is a versatile technology that can be used with both organic and inorganic acids. This implies that the electrolyte used in New Sky Energy process could be selected to optimise both raw material cost and the value of the produced acid.

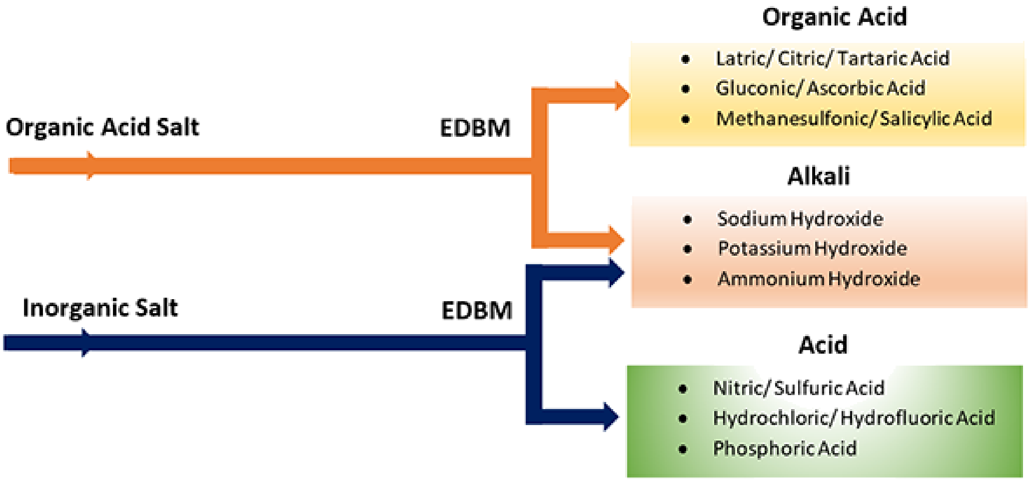

Figure 57: *Possible product splits available using EPDM* [113]

As of November 2021, New Sky Energy was yet to commercialise the CarbonCycle but was conducting pilot projects at several sites. It collaborated with St. Gobain, a French glass manufacturer, to conduct a pilot project capturing CO_2 to produce baking soda for glass manufacturing. New Sky Energy claims that the carbon emissions associated with its sodium bicarbonate product are reduced by up to one-third compared to the conventional process. The

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[112] https://www.lenntech.com/processes/bipolar-membrane-electrodialysis-edbm-.htm

[113] https://www.lenntech.com/processes/bipolar-membrane-electrodialysis-edbm-.htm

CarbonCycle process was also deployed at Avery Brewing, to capture CO_2 and convert it into sodium bicarbonate, which could ultimately be recycled into the glassmaking process.[114]

7.4.2 ACI Comments

The processes discussed in this section are very prospective, for a number of reasons. Firstly, Australia now relies on imported supplies of sodium carbonate and sodium bicarbonate, so there is an opportunity to use captured CO_2 to produce these chemicals locally. Importantly, the Skyonic/CarbonFree SkyMine® process has demonstrated that this can support a commercially-viable stand-alone business, which is quite unusual.

Secondly, the discovery by MIT researchers that sodium bicarbonate can substitute for 20% of Portland cement in a concrete mix, and reduce overall CO_2 concrete emissions by 15% (Section 7.1.3.1.5), indicates the potential to permanently and conveniently sequester large quantities of captured CO_2 in concrete structures. If this can be validated through concrete performance trials, this would be the single largest opportunity for CO_2 recycle identified in this report.

Thirdly, the Skyonic/CarbonFree and New Sky Energy processes demonstrate that sodium hydroxide can be produced by electrolysis of simple salts using renewable energy. Recall that in the Calera process (Section 7.1.1.1) CO_2 is captured by reacting with hydroxide to form sodium bicarbonate/carbonate, which is immediately reacted with a source of Ca^{2+}/Mg^{2+} ions to form insoluble $CaCO_3$/$MgCO_3$.

In the Latrobe Valley there is an enormous reservoir of Ca/Mg in the form of power station fly ash, which is currently sitting bunded and covered with earth, with the only immediate prospect of rehabilitation being the Latrobe Magnesium pilot plant (Section 7.1.2.3.2). Fly ash from the operation of Loy Yang A and B power stations would be of the order of 10 million tonnes, not to mention the ash from the Hazelwood and Yallourn power stations. The ability to cost-effectively produce hydroxide locally could underpin a new industry sector based on upgrading fly ash with captured CO_2.

The Skyonic/CarbonFree SkyMine® process generates NaOH from NaCl using a conventional chlor-alkali electrolysis process. This has the disadvantage of also producing H_2 and Cl_2, which are hazardous materials, although this problem is obviated by immediately transforming them into hydrochloric acid (HCl) and bleach (NaClO) as saleable products. In contrast, the New Sky Energy CarbonCycle process uses EDBM, which produces only separate streams of acid and alkali.

The Skyonic/CarbonFree process is currently subject to active patent coverage in Australia, while New Sky Energy's process was never subject to an Australian patent application. There is thus an opportunity to devise a process utilising EDBM to integrate with local resource availability.

For example, New Sky Energy uses sodium sulphate as an electrolyte salt, which is split by EDBM to form sodium hydroxide and sulphuric acid. The NaOH could be reacted with CO_2 to produce sodium carbonate or sodium bicarbonate, which could be sold locally and/or incorporated into concrete

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[114] https://sp-edge.com/companies/180640

materials. Alternatively, some or all of the bicarbonate solution could be reacted with fly ash to produce precipitated Ca/Mg carbonates, which could then be used to manufacture 'green' plasterboard for construction use. The sulphuric acid by-product could be sold locally, or could be reacted with locally-produced blue ammonia to produce ammonium sulphate, which is widely used as a fertiliser.

EDBM membranes are commercially produced by FuMA-Tech GmbH (Germany), Solvay SA (Belgium), Tokuyama Co. (Japan), WSI Technologies Inc. (U.S.), Graver Water Co. (U.S.), and Tianwei Membrane Technology Co. Ltd. (China) (Huang & Xu 2006), and are employed in water treatments systems offered in Australia by MAK Water[115] and CELSA ElectroFlow Technologies.[116]

The EDBM process should thus be regarded as a key enabling technology for new manufacturing opportunities in the Latrobe Valley, being commercially available and apparently unencumbered by patent restrictions for carbonate production. As such, this is a topic that merits further investigation for deployment in Victoria.

7.5 SUMMARY COMMENTS ON INORGANIC CARBONATION

The range of chemistries and technologies that have been developed to exploit inorganic carbonation is a testament to the versatility and commercial potential of this route. The various technologies described above can be categorised as utilising four different carbonation strategies:

a) Reaction of CO_2 with the Ca^{2+} and/or Mg^{2+} sites naturally present in a solid substrate, binding the CO_2 as a surface coating on the substrate – i.e., Carbon8 Systems, SequesTech, Solidia, Carbicrete, CarbonBuilt, CarbonCure.
b) Reaction of CO_2 with a solution of Ca^{2+} and/or Mg^{2+}, producing a precipitate of solid $CaCO_3$ and/or $MgCO_3$ – i.e., Carbon Engineering, EnPro.
c) Reaction of CO_2 with NaOH to produce sodium bicarbonate (or carbonate), which can be:
    i. An end product in itself -i.e., Skyonic/CarbonFree, New Sky Energy.
    ii. Further reacted with Ca^{2+} and/or Mg^{2+} to form solid $CaCO_3$ and/or $MgCO_3$ – i.e., Calera/Fortera, Carbon Capture Machine
d) Reaction of CO_2 with ammonium to produce either ammonium bicarbonate, which is then further reacted with Ca^{2+} and/or Mg^{2+} (solubilised from a solid subrate using ammonium) to form solid $CaCO_3$ and/or $MgCO_3$ – i.e., Blue Planet, Slag2PCC, Monash University.

These options provide great scope to develop novel reaction systems to utilise any suitable low-cost raw materials that are locally available (usually industrial waste) and transform them into new business opportunities.

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[115] https://www.makwater.com.au/mega-partners-with-mak-water-as-exclusive-oceania-distributor-of-electro-membrane-water-technologies/
[116] https://celsa.com.au/electrodialysis-ed

Many of the technologies that have been reviewed here have successfully passed through the R&D phase and have been commercialised. CarbonCure has standardised its system for injection of CO_2 into concrete slurry and sold more than 650 units in thirty countries, producing about 5 million truckloads of low-carbon concrete. This technology is now available in Australia through CarbonCure's partnership with BOC Gases. Systems for producing low-carbon concrete blocks, slabs, pavers and tiles have been commercialised by Solidia, Carbicrete, CarbonBuilt. Carbon8 Systems has commercialised its process for direct carbonation of solid wastes, and Blue Planet has commercialised its process for continuous extraction of Ca/Mg from solids and precipitation as Ca/Mg carbonates. CarbonFree has commercialised its process for producing baking soda using hydroxide extracted from low-cost salts.

These processes are all capable of incorporating captured CO_2 into low-emissions products, mostly for the construction sector, including concrete formwork, pre-formed concrete blocks, slabs, etc., insulation and plasterboard. This is an ideal way to foster a low-emissions economy, because the captured CO_2 is permanently sequestered into valuable products in a sector that is large and continually growing.

Moreover, the processes involved in inorganic carbonation are also directly applicable to direct air capture (DAC) of CO_2, which will also need to expand rapidly in the near future. There are presently 19 DAC plants operating worldwide, capturing only around 0.01 Mt CO_2/year (Ozkan et al. 2022). Most DAC systems capture CO_2 using aqueous solutions of potassium hydroxide or sodium hydroxide, but regenerating the alkali requires high temperatures (> 900 ^oC) and are energy-intensive (Sodiq et al. 2023). There would appear to be opportunities to integrate some of the inorganic carbonation technologies with DAC, to simultaneously capture CO_2 and transform it into valuable Ca/Mg carbonate products for the construction industry. This would create an economic incentive for DAC and couple its growth to the burgeoning construction sector.

Inorganic carbonation is an active area of development overseas but, apart from the Monash University work, there does not seem to be anything being done in Australia. Based on overseas experience, there is clearly scope for the creation of new local industries to take advantage of the move toward low-carbon products, particularly for the construction sector.

As such, inorganic carbonation is an area of R&D that urgently needs to be kick-started in Australia. Coordinated research by both industry and academia is required, supported by policy direction from the government. The scale of the opportunity is significant. The Cement, Concrete, Sand and Aggregate Association estimate that Victoria will require 8 tonnes of aggregate construction material per person in Victoria,[117] equating to around 100 million tonnes of concrete used in the state each year.[118] In 2020-21, greenhouse gas emissions from the Victorian 'Industrial Process and Product

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[117] https://www.ccaa.com.au/common/Uploaded%20files/CCAA/Policy/Policy%20Priorities/VIC_Policy_Priorities_2018.pdf

[118] Concrete comprising 3 parts aggregate, 2 parts sand and 1 part cement

Use' sector totaled 3.94 Mt, or 5% of the state total.[119] The Victorian government is working to reduce emissions in this sector through its Big Build projects. For example, Rail Projects Victoria, the agency delivering the Metro Tunnel, has committed to a 36% reduction in the Portland cement content of concrete across all its construction projects. This is being accomplished by supplementation with black coal fly ash and blast furnace slag,[120] which are sourced from NSW and Qld.

Victoria is well placed to produce its own cement substitutes, while solving environmental problems at the same time. The power stations in the Latrobe Valley have produced tens of millions of tonnes of Ca/Mg-rich fly ash, which is sitting in bunded dams awaiting reclamation. It would be a relatively simple matter to upgrade this fly ash into a supplementary cementitious material, turning a waste disposal problem into a new revenue stream for the power companies. The fly ash could be further value-added by solubilising the Ca/Mg components for reaction with CO_2 or sodium bicarbonate, with possible separation of the Ca and Mg components, to produce Ca, Mg or Ca/Mg carbonates as individual products.

Also, Boral's Blue Circle Southern cement works in Waurn Ponds produces cement kiln dust as a by-product. Modular CO_2 capture systems are now available (e.g., Carbon Clean[121], Aker Carbon Capture[122], Mitsubishi Heavy Industries[123]) that could be used to capture CO_2 emissions from the kiln flue gas for carbonation of the kiln dust. This combination would make the cement from Blue Circle Southern close to carbon neutral.

Injection of captured CO_2 into fresh concrete has the potential to reduce the State's consumption of cement by about 1.3 Mt, eliminating 1 Mt of CO_2 emissions (Grant 2015). Most of the cement consumed in Victoria is sourced from NSW and SA, so the emissions associated with cement manufacture form a minor part of Victoria's GHG emissions. In the local context, 1 Mt CO_2-e emissions reduction is equivalent to taking 11%, or ~350,000, cars off Victoria's roads.[124]

Inorganic carbonation has the potential to make a significant contribution to both the Victorian economy and the State's ambition to reach net zero by 2045. Given the lack of current activity in this area, it is clear that the potential of this technology will not be realised in Victoria without a coordinated effort involving government, industry and research organisations. It is recommended that this be undertaken as a matter of high priority.

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[119] https://view.officeapps.live.com/op/view.aspx?src=https%3A%2F%2Fwww.dcceew.gov.au%2Fsites%2Fdefault%2Ffiles%2Fdocuments%2Fageis-state-territory-inventories-2021-sectoral-breakdown-data-tables.xlsx&wdOrigin=BROWSELINK

[120] https://bigbuild.vic.gov.au/projects/metro-tunnel/about/sustainability/initiatives/reducing-carbon-emissions-in-concrete/portland-cement-reduction

[121] https://www.carbonclean.com/modular-carbon-capture-systems

[122] https://akercarboncapture.com

[123] https://www.mhi.com/products/engineering/co2plants_process.html

[124] https://www.infrastructurevictoria.com.au/wp-content/uploads/2021/08/Driving-Down-Emissions-Accelerating-Victorias-Zero-Emission-Vehicle-Uptake.pdf; https://www.abs.gov.au/statistics/industry/tourism-and-transport/motor-vehicle-census-australia/latest-release

8 Catalytic Chemical Conversion of CO_2

This section includes chemical processes for CO_2 recycle that require a higher energy input than the processes described above, needing efficient catalysts to help overcome the energy barrier to break C=O bonds. This includes the production of valuable organic carbonates (linear, cyclic, polycarbonate polyols and polymers) and a wide variety reaction intermediates and fine chemicals.

This section also includes processes that involve the catalytic reduction of CO_2 with hydrogen. This requires even higher energy, but can be used to synthesise valuable commodities such as formic acid, methanol, carbon monoxide, synthesis gas, methane (synthetic natural gas) and hydrocarbon olefins and fuels.

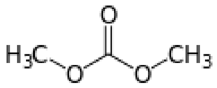
8.1 ORGANIC CARBONATES

8.1.1 Introduction to Organic Carbonates

Organic carbonates are promising candidates as “green” replacements for conventional noxious solvents and fuel additives, as well as for the development of innovative intermediates in the pharmaceutical, lubricant and polymer industries.

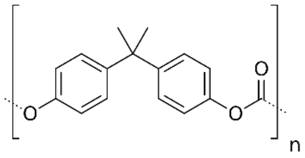
Organic carbonates are a very large group of compounds, characterised as being esters of CO_2, or ‘anhydrous carbonic acid’. They consist of a carbonyl group flanked by two alkoxy groups, with the general structure $R_1O(C{=}O)OR_2$. There are two classes of organic carbonate: linear (or acyclic) and cyclic carbonates.

The simplest linear carbonates contain two identical substituents; depending on whether the substituents are aliphatic or aromatic, they are called dialkyl or diaryl carbonates, respectively. The simplest members of these classes are dimethyl carbonate and diphenyl carbonate.



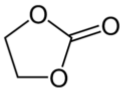
Dimethyl carbonate

In the more complex linear polycarbonates, two carbonate groups can be linked by an aliphatic or aromatic bifunctional group, forming polymers such as Lexan (bisphenol A polycarbonate).



Bisphenol A polycarbonate (BPA-PC)

In cyclic carbonates, the carbonate groups are linked by a 2- or 3-carbon bridge.



Ethylene carbonate

The four most industrially useful organic carbonates are dimethyl carbonate (DMC), diphenyl carbonate (DPC), ethylene carbonate (EC) and propylene carbonate (PC). The main uses for organic carbonates are (Sakakura & Kohno 2009):

- Production of engineering plastics such as polycarbonates and polyurethanes;
- Electrolyte solvents for lithium-ion batteries;
- Organic solvents with high solubilising power and relatively low toxicity;
- Fuel additives to increase octane value, reduce carbon particulates and fouling; and
- “Green” reagents in chemical syntheses and industrial products (e.g., degreasing, paint stripping, cleaning), as a substitute for various toxic chemical reagents. EC and PC are biodegradable, have high solvency, high boiling and flash points, low odour levels and evaporation rates, and low toxicities (Clements 2003).

8.1.2 Linear Organic Carbonates

8.1.2.1 Current Status

The most common and successful method for producing organic carbonates, including polycarbonates, has been based for a long time on the reaction between and alcohol and phenol with phosgene ($COCl_2$).

Phosgene is highly reactive and versatile, giving high yields under mild conditions. Around 2 million tonnes of polycarbonate is produced each year using this method (Sakakura & Kohno 2009). However, phosgene is lethally toxic, so safer methods have been progressively developed; all of them being catalytic (Ballivet-Tkatchenko & Sorokina 2003). The most significant processes that have been commercialised involve the production of:

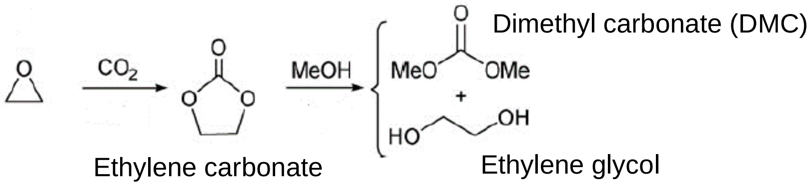
- DMC via the oxidative carbonylation of methanol with CO, with copper chlorides as catalyst precursors (EniChem and Ube Industries processes). This is the current state of the art commercial process for DMC production.
- DPC by transesterification of DMC and phenol, catalysed by titanium alkoxides (EniChem process).
- BPA-PC by transesterification of BPA and DPC in the presence of basic catalysts (General Electric Plastic process).
- Poly(alkylene carbonate) via the transesterification of cyclic carbonates with ethylene or propylene oxide and CO_2, catalysed by zinc derivatives with hydrogen donor co-catalyst (Asahi Kasei Chemicals process). This was the first polymer production involving the direct

use of CO_2 and is one of a few successful examples of exploitation of CO_2 in the chemical industry (Ballivet-Tkatchenko & Sorokina 2003).

By the end of the 1990s, the two largest phosgene-free processes were the EniChem process and the Ube Industries process, both based on the incorporation of carbon monoxide and methanol by transition metal catalysts. Although safer than the phosgenation of methanol, these synthetic routes still involved poisonous carbon monoxide and methyl nitrite, and chlorine-based catalysts (Selva et al. 2016).

8.1.2.1.1 Asahi Kasei process

The growth of the world market for CDs, DVDs and mobile phone cases, which are fabricated from Bisphenol A polycarbonate (BPA-PC), led to investment in new organic carbonate capacity in Asia and the development of improved methods. In 2002, Asahi Kasei Chemicals unveiled a new process for producing BPA-PC monomer using CO_2 for the synthesis of DMC as an intermediate. The first step is the insertion of CO_2 into ethylene oxide to give ethylene carbonate (EC). The second involves the transesterification of EC with methanol, producing DMC and ethylene glycol.



The reaction is carried out in a continuous distillation reactor loaded with a quaternary ammonium strongly basic anion exchange resin and alkali hydroxides, yielding DMC in practically quantitative yields.

The third step is the transesterification of DMC with phenol by a catalytic reactive distillation in the presence of a homogeneous Ti, Bu-Sn or Pb catalyst, yielding diphenyl carbonate (DPC) and methanol in high purity. The fourth step, DPC reacts with bisphenol-A to produce BPA-PC and phenol, using a novel reactor designed for optimum process control (Fukuoka et al. 2010). The overall scheme of the Asahi Kasei process is shown in Figure 58 below:

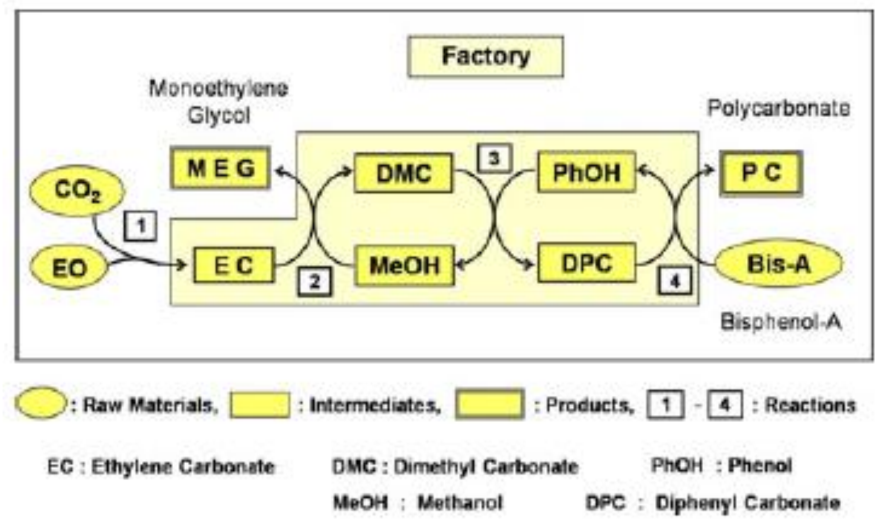


Figure 58: *Asahi Kasei process for producing polycarbonate (Fukuoka et al. 2010).*

The Asahi Kasei process is totally green, because not only is CO_2 from the atmosphere being effectively utilised, but all intermediate products – ethylene carbonate (EC), dimethyl carbonate (DMC), methanol, diphenyl carbonate (DPC), and phenol – are completely used up or recycled as raw material for the next or preceding reaction. There is no waste, no waste process water necessary for disposal-treatment, and materials-savings and energy-savings are all achieved. There are at least five commercial plants utilising this process, in Taiwan (150,000 t/y), Korea (2 plants of 65,000 t/y), Russia (65,000 t/y) and Saudi Arabia (260,000 t/y) (Fukuoka et al. 2010).

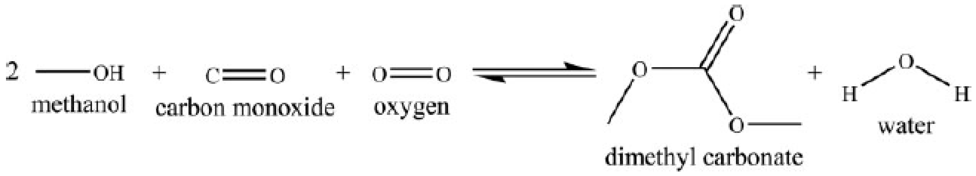
The Asahi Kasei process highlights the fact that the synthesis of DMC by transesterification of ethylene carbonate with methanol does not necessarily require transition metal catalysis as do the EniChem and Ube processes. Instead, the reaction can be effectively catalysed by a combination of supported basic ammonium resins and homogeneous alkaline bases, thereby demonstrating the potential of transition metal-free catalytic systems for the synthesis and the further transformation of organic carbonates (Selva et al. 2016).

8.1.2.1.2 Dimethyl Carbonate

DMC, the simplest organic carbonate, has an important role in chemical industry due to its versatility and large range of applications. Its low toxicity for human health makes DMC in a ‘green’ chemical for sustainable processes. DMC has many applications as an industrial solvent, based on its low viscosity, low toxicity, and its good solvency power. DMC is also a valuable building block for many organic synthesis, especially for carbonylation and methylation reactions, being an eco-friendly replacement for the current hazardous chemicals phosgene and dimethyl sulfate, respectively. In addition, DMC is an important solvent for lithium ion batteries, and is valuable alternative to the additive methyl-*tert*-butyl ether in gasoline and diesel (Santos et al. 2014).

Despite the success of the EniChem, Ube Industries and Asahi Kasei processes for synthesis of DMC without the use of phosgene, the industrial value of DMC is such that many alternative processes have been developed. Transesterification of cyclic carbonates, transesterification of urea, carbonylation of methanol, and oxidation of dimethoxy methane have all been investigated. These have been previously reviewed (Santos et al. 2014) and will not be discussed in detail here.

The simplest of all the routes for DMC synthesis is the direct conversion of methanol and carbon dioxide, producing dimethyl carbonate and water.



This route promotes the consumption of CO_2, which is nontoxic, nonflammable, noncorrosive, and abundant. Methanol has low toxicity compared to the chemicals used in the other routes and is economically attractive. However, the low reaction rate and high thermodynamic limitations are the main barriers to the industrial implementation of this route.

This has prompted researchers worldwide to investigate improved catalyst systems for facilitating this reaction. These developments have been thoroughly reviewed (Santos et al. 2014). $Ce_xZr_{(1-x)}O_2$-based catalysts have been shown to exhibit high activity and selectivity, and *in situ* water removal agents, such as molecular sieves, ketals, epoxides, and nitriles can enhance the DMC yield. This remains an active area of research.

8.1.2.2 Victorian Research Context

ACI is not aware of any relevant local research in this area.

8.1.2.3 ACI Comments

For the production of methanol from CO_2 (see Section 8.3.5 below), it has been suggested that it is necessary to upgrade the methanol to higher-value products, such as DMC or dimethyl ether (DME), in order to be financially attractive. There is high international interest in the production of methanol using recycled CO_2, which suggests that cost-effective routes from methanol to DMC should also be on the research agenda.

8.1.3 Cyclic Organic Carbonates

8.1.3.1 Current Status

Cyclic organic carbonates are useful reactive intermediates that are used industrially for preparation of monomers, polymers, surfactants, plasticizers, cross-linking agents, curing agents and solvents (Clements 2003). Cyclic carbonates are receiving growing industrial interest because their preparation and applications are attractive in the context of green chemistry and sustainability. Annual production of cyclic carbonates is around 100 kt/y (Kamphuis et al. 2019).

The main route used for the synthesis of the major cyclic organic carbonates, ethylene carbonate (EC) and propylene carbonate (PC), is by cycloaddition of CO_2 with epoxides, typically using an alkylammonium halide catalyst such as tetraethylammonium bromide (Clements 2003), as shown in Figure 59 below. In this process, the product also becomes the reaction solvent. This reaction occurs easily because of the high energy level of the epoxides. Synthesis of cyclic organic carbonates produces a minimum amount of waste, resulting in a low environmental impact (Wang et al. 2016a).

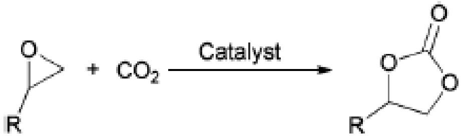


Figure 59: *Cycloaddition reaction of* CO_2 *with epoxides. R = H,* CH_3 *or* C_2H_5 *(Clements (003)*

This is an important and versatile reaction for the direct synthesis of products from CO_2. A wide variety of epoxides may be employed in this reaction, which allows versatile and tunable chemical reactivity depending on reaction conditions. Cyclic organic carbonates can be synthesised that contain active moieties such as alkyl, alkoxy, and carbonyl groups. Consequently, they can serve as chlorine-free reagents in alkylation, hydroxyalkylation, and carbonylation reactions in place of dangerous phosgene, methyl halides and dimethyl sulphate (Wang et al. 2016). The catalysts that have been investigated for these reactions have been reviewed by North et al. (2010).

Cyclic organic carbonates can react with aliphatic and aromatic amines, alcohols, thiols and carboxylic acids, to create a range of important products. Each of these is briefly discussed below.

8.1.3.1.1 Reactions with aromatic amines, alcohols and thiols

Cyclic carbonates can be used to alkylate active-hydrogen-containing aromatics such as phenol and phenolic resins, thiophenols, aniline, and the like in the presence of alkali catalysts. While these reactions can also be achieved using epoxides, the use of cyclic carbonates is far less hazardous and requires lower pressure. Most importantly, alkylation using cyclic carbonates does not require the use of a solvent, as the carbonate acts as both reactant and as solvent (Clements 2003).

8.1.3.1.2 Reactions with carboxylic acids

The reaction between cyclic carbonates and carboxylic acids is important for the polymers industry. For example, researchers at Reichhold reacted EC and PC with multifunctional carboxylic acids such as terephthalic acid to synthesise polyester oligomers, which were then reacted with simple diols and unsaturated anhydrides to give unsaturated polyesters useful in composites for the aerospace industry. Researchers at Cape Industries reacted PC with poly(ethylene terephthalate) (PET) to make it more suitable for use in producing polyurethane foams. Researchers at Stockhausen used cyclic carbonates to crosslink sodium polyacrylate to produce a superabsorbing medium for use in sanitary articles (Clements 2003).

8.1.3.1.3 Reactions with aliphatic alcohols and the synthesis of polycarbonates

Cyclic carbonates react with aliphatic alcohols differently than with their aromatic analogues. Whereas EC reacts with phenol to yield 2-phenoxyethanol via alkylation and loss of CO_2, EC reacts with methanol by the transesterification route to produce the dialkyl carbonate DMC.

Cyclic carbonates can also be reacted with diols to form other alkene carbonates or polycarbonates, as shown in Figure 60 below.

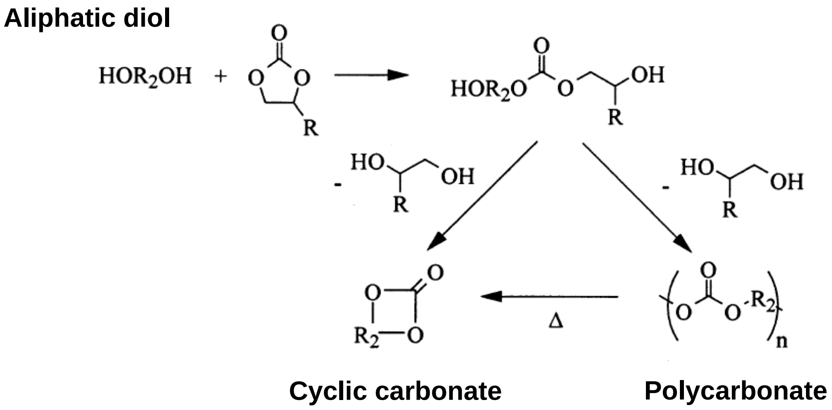
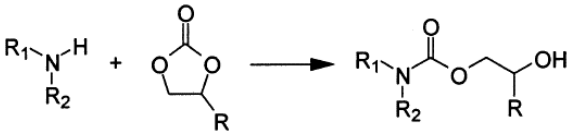


Figure 60: *Reactions between cyclic carbonates and aliphatic diols (Clements 2003)*

Polycarbonates produced in this manner have high tensile strength, flexibility and chemical resistance, making them useful in the manufacture of paints, coatings and adhesives (Clements 2003).

8.1.3.1.4 Reactions with aliphatic amines

As with aliphatic alcohols, cyclic carbonates react very differently with aliphatic amines than with their aromatic analogues. They undergo attack at the carbonyl carbon atom followed by ring-opening to give a urethane (carbamate) product, useful as a reactive intermediate.



In addition to polyurethanes, the above approach has also been applied to the modification of amino acids for the production of biocompatible polymers, and dispersants for use in lubricating oils, hydraulic oils and gasoline (Clements 2003).

8.1.3.2 C4X

The Chinese company, C4X, is using cyclic organic carbonate chemistry as a route to the low-cost production of methanol. A two-step process is involved. In the first, purified flue gas with a high CO_2 concentration is heated with ethylene oxide and a cheap aluminium or copper oxide-based catalyst to create ethylene carbonate. The ethylene carbonate is then reacted with hydrogen using a Ru pincer catalyst to produce ethylene glycol and methanol, as shown in Figure 61 below.[125]

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[125] https://www.wired.co.uk/article/xprize-global-warming-climate-change-co2-pollution

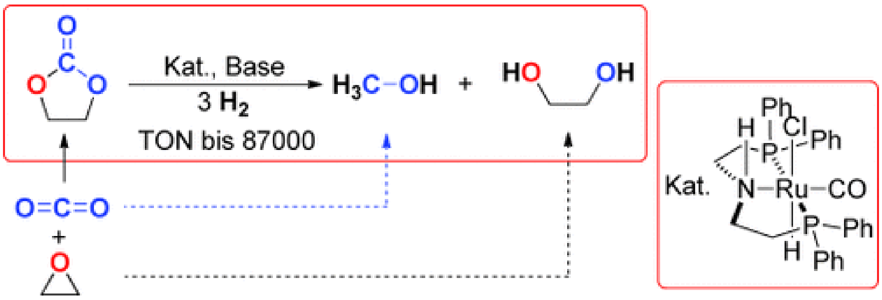


Figure 61: *Two-step conversion of CO_2 to methanol via ethylene carbonate (Han et al. 2012)*

It has been reported that the conversion to methanol proceeds smoothly with 0.001 % catalyst loading at 140 °C, producing methanol and ethylene glycol at >99 % yield within 1 hour (Li et al. 2013). C4X is currently scaling up its process at the Wyoming Integrated Test Center. The technology is at the commercial pilot scale, with a TRL of 6 – 7.

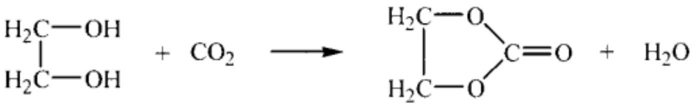
C4X is pursuing a combination of licensing and strategic corporate investment to scale and deploy their systems. In China, C4X has partnered with CONCH, the largest cement maker in China, as well as SinoChem, Huaneng Power, Jinhong Gas, Wanli Group. In Canada, C4X has partnered with Ford Motor Company of Canada, Walkerville Brewery, and others to produce automotive interior parts, ethylene carbonate for Li-ion batteries, and ethylene glycol for polyester.[126]

8.1.3.3 Victorian Research Context

The two major cyclic organic carbonates, ethylene carbonate (EC) and propylene carbonate (PC) are widely used as solvents, industrial lubricants, electrolytes for lithium-ion batteries, and precursors for polycarbonate synthesis. They have attractive features such as high boiling and flash points, with low toxicity.

Of the two, ethylene carbonate is the preferred solvent for use in lithium-ion batteries. The growing demand for electric vehicles is driving growth in the global market for EC, which is expected to grow from US$288 million in 2019 to US$418.5 million in 2027 (Parihar & Prasad 2020).

However, the current industrial process for EC synthesis involves reaction of CO_2 with ethylene oxide, which is a toxic petrochemical (Clements 2003). As an alternative, Professor Sankar Bhattacharya, at Monash University, is investigating the synthesis of ethylene carbonate by direct carboxylation of ethylene glycol:



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[126] https://carbon.xprize.org/prizes/carbon/articles/finalist-team-profiles

Ethylene glycol (EG) can be readily synthesised from glycerol, which is a byproduct of the biodiesel and soap manufacturing industries, so production of EC by carboxylation of EG is an attractive renewable pathway (Ng et al. 2023).

The research at Monash University is aimed at overcoming the key challenge associated with this reaction pathway, which is end-product limitation due to accumulation of water as byproduct. The experimental strategies being investigated, shown in Figure 62 below, include catalyst synthesis on a 3-D printed support, continuous flow operation and continuous removal of water by sparging with CO_2 (Ng et al. 2023).

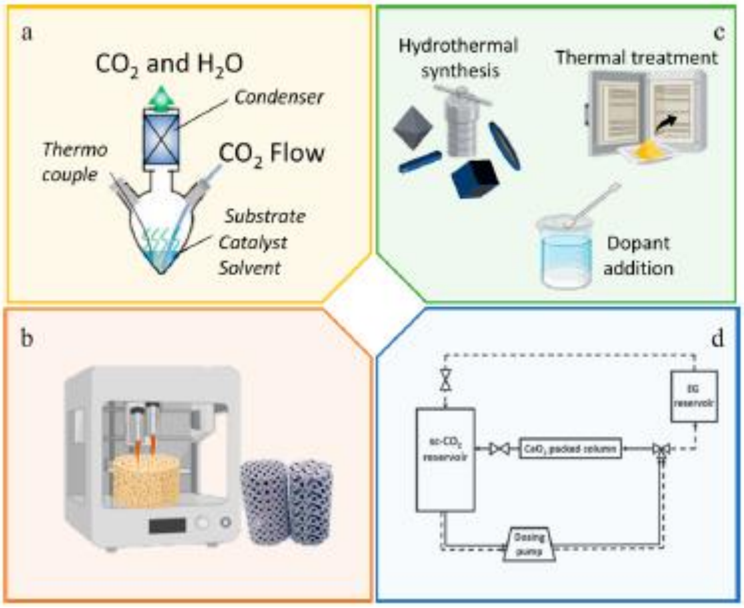

Figure 62: *Experimental strategies to overcome the limitations of EC production by carboxylation of EG. (a) Continuous removal of* H_2O *by gas stripping; (b) 3D-printed catalyst; (c) Catalyst morphology control; (d) Continuous-flow reaction (Ng et al. 2023).*

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8.1.3.4 ACI Comments

The research on ethylene carbonate synthesis at Monash University is novel and at the forefront of international research in this field. Given the growing demand for its use in lithium-ion batteries, and the desirability of using renewable feedstocks, continued research toward scale-up of this technology is recommended.

8.1.4 Polycarbonate Polyols and Polymers

8.1.4.1 Current Status

Polycarbonate compounds can be synthesised by reacting CO_2 with bifunctional epoxides, as shown in Figure 63 below.

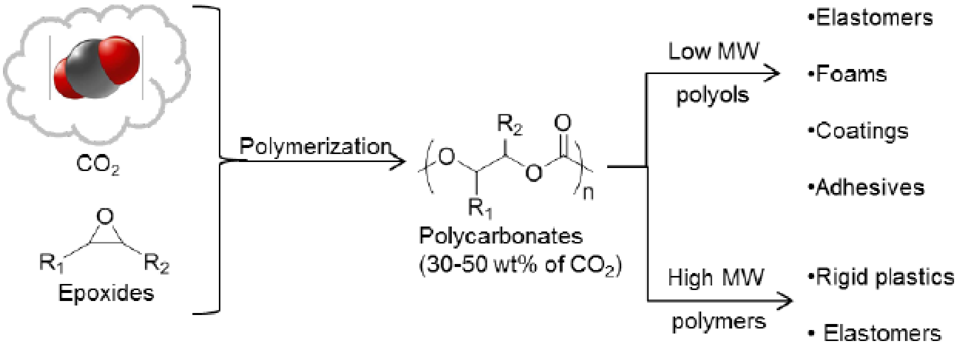


Figure 63: *Recycling carbon dioxide into valuable polycarbonates (Xu et al. 2016)*

This is a very versatile chemistry, which can be used to synthesise a range of commercially valuable products and intermediates. This represents a new and very important avenue for conversion of CO_2 into value-added products.

As shown in Figure 63, there are two main classes of product that can be synthesised by carbonation of bifunctional epoxides: polycarbonate polyols and polycarbonate polymers. The term 'polyol', in general, refers to a compound containing two or more alcohol (-OH) functional groups, so polycarbonate polyols contain numerous primary- and/or secondary-functionalised alcohol moieties. Polycarbonate polyols are typically liquids of relatively low molecular weight, while polycarbonate polymers are rigid solids.

The industrial development of polycarbonates is still in its early days, with progress dependent on the availability of suitable catalysts. There has been a variety of types of catalyst developed for the copolymerisation of CO_2 and epoxides, either heterogeneous or homogeneous. Typical heterogeneous catalysts include Zn/ET_2/active hydrogen-containing compound systems, carboxylic zinc, double metal cyanide complexes and rare-earth metal coordination ternary catalysts. Typical homogeneous catalysts are metal porphyrins, zinc phenolate, discrete β-diiminate zinc, and binary or single bifunctional catalysts systems based on metal-salen or –salen complexes. The development of these catalyst systems is reviewed elsewhere (Qin & Wang 2010; Qin et al. 2015; Bahramian et al. 2016) and is not the subject of this report.

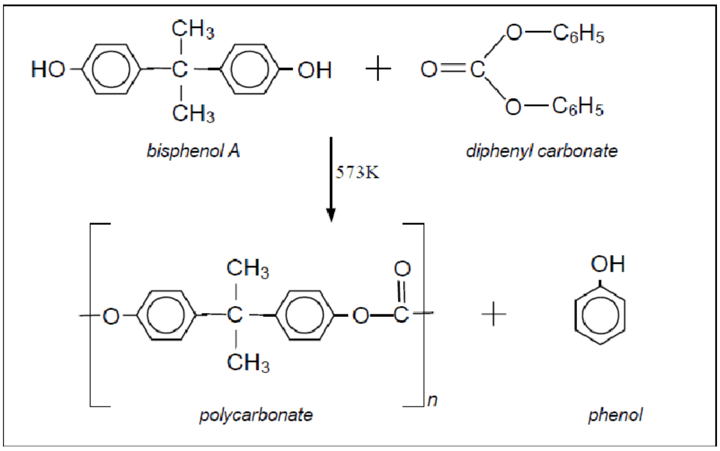
The development of improved catalysts has allowed the commercial development of polycarbonates using CO_2 as a raw material. Due to its commercial significance, this is a very active area of research which cannot be fully surveyed in a report of this nature. Instead, three main product categories will be discussed: (i) polycarbonate polymers, (ii) polyols, and (iii) polyurethanes (being an application of the first two). Each of these are discussed below.

8.1.4.1.1 Polycarbonate polymers

The versatility of the polycarbonate synthesis route is such that a wide range of polycarbonate polymers can potentially be made. From a commercial point of view, the most significant at the present time is Bisphenol A polycarbonate, although poly(butylene carbonate) (PBC), poly(ethylene carbonate) (PEC), poly(propylene carbonate) (PPC) and poly(cyclohexadiene carbonate) (PCHC) are considered to have major industrial potential. These polymers are thermoplastic, transparent, UV stable, biodegradable and have good electrical insulation. They are of great interest for applications in the electronics, industrial packaging, agricultural mulch films, foams, biomedical and health care sectors (Muthuraj & Mekonnen 2018).

8.1.4.1.1.1 Bisphenol A polycarbonate

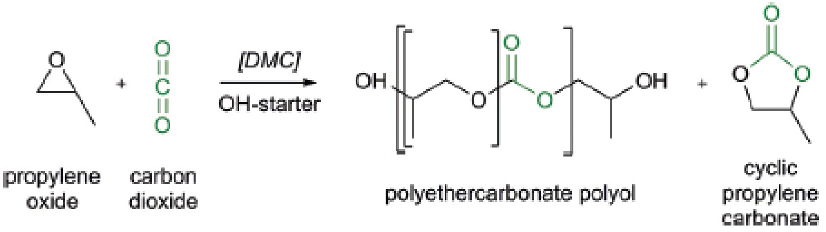
Bisphenol A polycarbonate (BPA-PC), better known as Lexan, is the major polymer currently produced from CO_2, in the process developed by Asahi Kasei Chemicals (Fukuoka et al. 2010). It is highly impact-resistant and optically transparent, and is used in CDs, DVDs, eyeglasses lenses, aircraft windows, smartphone cases, etc. The basic reaction concept utilised in the Asahi Kasei BPA-PC process is:



In the Asahi Kasei process, the phenol by-product is recycled to produce the reaction intermediate diphenyl carbonate. This is currently the dominant route for production of BPA-PC, with total global production of 750,000 t/y (Ruiz et al. 2021).

8.1.4.1.1.2 Poly(propylene carbonate)

Poly(propylene carbonate) (PPC) is formed from the reaction between CO_2 and propylene oxide. Catalysts developed for this reaction have been reviewed elsewhere (Muthuraj & Mekonnen 2018a; Xu et al. 2018).



PPC is biodegradable and biocompatible and has excellent oxygen barrier properties. It can be processed by all major thermoplastic processing techniques, such as injection moulding, blow moulding, blown films, extrusion film casting, compression moulding, solvent casting, spin casting and electrospinning (Muthuraj & Mekonnen 2018a). These qualities have allowed PCC to be utilised for production of barrier films, foam packaging, electromagnetic shielding, energy storage, disposable goods and binders, and in the production of polyurethane emulsion and foam. It is also being investigated for biomedical applications such as drug delivery, drug-eluting stent coating and tissue scaffold materials (Xu et al. 2018).

The main commercial producers of PPC are:

- Mengxi High-tech Group has a 1000 t/y PPC production facility in Erdos, Inner Mongolia, which makes use of a rare earth metal ternary catalyst developed by the Changchun Institute of Applied Chemistry. CO_2 is captured from cement kiln exhaust gas and converted into PCC for use in products such as medical dressings and biodegradable packaging films (Qin & Wang 2010).
- Tianguan Group in Henan, China, uses a low cost zinc carboxylate catalyst to produce PPC from waste CO_2 from an alcoholic fermentation process. Production capacity reached 25,000 t/y in 2012 (Xu et al. 2018).
- Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, developed a zinc-based catalyst (Zhao et al. 2009), which is used under license to produce 30,000 t/y PPC by Taizhou BangFeng Plastic Co in Taizhou (Ruiz et al. 2021), and 50,000 t/y PPC by Boda Dongfang Group Co. (Hong Kong) in Jilin (Cao & Wang 2021).
- SK Innovation, Korea, has commercialised a PCC product called GreenPol™, using a cobalt catalyst system acquired from Ajou University (Qin & Wang 2010; Jeong et al. 2015).
- Empower Materials, USA, produces poly(alkylene carbonate) copolymers (PPC, poly(ethylene carbonate) and poly(cyclohexene carbonate)), which are used in a variety of industrial pastes and binders.

Further development of PPC and other polycarbonate products is dependent upon development of improved catalyst systems. The current catalysts have relatively low efficiency compared to those used industrially for polyolefin production, which is why this remains an active field of research (Xu et al. 2018).

PPC has some other issues that limit its commercial development, include low thermal degradation temperature, low mechanical strength and poor dimensional stability. Some of these issues can be attributed to the presence of high levels of residual zinc catalyst in the polymer, which has been reported at 2500 ppm (Bahramian et al. 2016). The usual strategy to overcome these limitations is to increase performance by using PPC as a matrix component of polymer composites and nanocomposites. This topic has been reviewed by Muthuraj & Mekonnen (2018b).

Since 2016, trials have been conducted using 10 µm thickness PPC film as mulching film in for corn, tomato, onion, etc. Modified PPC film was blown using a conventional polyethylene film blowing machine, mechanically laid and in-situ punched for seed and fertilizer injection. The film remained intact in 45 days for cotton, 60 days for tomato, and 70 days for corn, according to the sunlight intensity and precipitation in different application areas (Cao & Wang 2021).

A company in Victoria, Cardia Bioplastics in Clayton, has been actively involved in the development of biodegradable polymers, particularly for use in compostable shopping bags. Currently, PPC is not regarded as compostable because of the high level of residual catalyst present (Muthuraj & Mekonnen 2018b). Cardia Bioplastics, through its subsidiary CO2Starch Pty Ltd, has commercialised a novel biodegradable PPC/starch composite for use in packaging, shopping bags, etc. (Chen & Scheirs 2011). CO2Starch collaborated with the University of Sydney to investigate strategies to lower the level of residual zinc catalyst. It was discovered that 90 % of the residual catalyst in PPC could be removed by extraction with CO_2-laden water at 70 bar and 45 ^oC, allowing the polymer to meet regulatory requirements for composting (Bahramian et al. 2016).

Fortuitously, it was found that this purification process increased the thermal decomposition temperature of PPC from 124 ^oC to 214 ^oC, which is of great importance for thermal processing such as hot-melt extrusion. It also increased the tensile modulus from 1 MPa to 1.4 MPa, which is significant for packaging and other applications (Bahramian et al. 2016). These results highlight that the commercial development of PPC is being limited by the current catalyst systems used in its production, and support the need for research into better alternatives.

8.1.4.1.1.3 Recyclable CO_2-based polycarbonates

A new development to be aware of, given the accumulation of waste plastics in the environment, is a focus on developing more sustainable new plastics, derived from CO_2 and biomass lignin, that are fully recyclable under mild conditions. This is mainly being driven by new resolutions and legal obligations from the European Commission. Efforts are being made to develop new plastics that can easily be degraded back to their original monomers or to high value-added products that can be upcycled (Siragusa et al. 2023).

A promising example of this approach is illustrated in Figure 64 below. It shows the co-polymerisation of 5,5’-(ethane-1,2-diyl)bis(4-hydroxy-3-(3-hydroxypropyl)-4,5-dimethyloxazolidin-2-one) with bis-exovinylene cyclic carbonate to form poly(oxo-carbonate)-co-(hydroxy-oxazolidinone), which can be decomposed under mild conditions to form mainly the starting monomer, which can be reused multiple times. Imine byproducts are also formed (not shown), which must be removed prior to recycling the monomer (Siragusa et al. 2022).

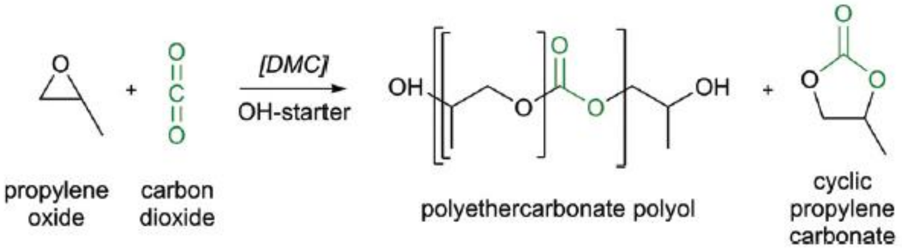
This type of research is still at an early exploratory stage, but is a topic of serious industrial interest with potential for valuable commercial developments.

Figure 64: *Example of a closed-loop polymerisation – depolymerisation system (Siragusa et al. 2022)*

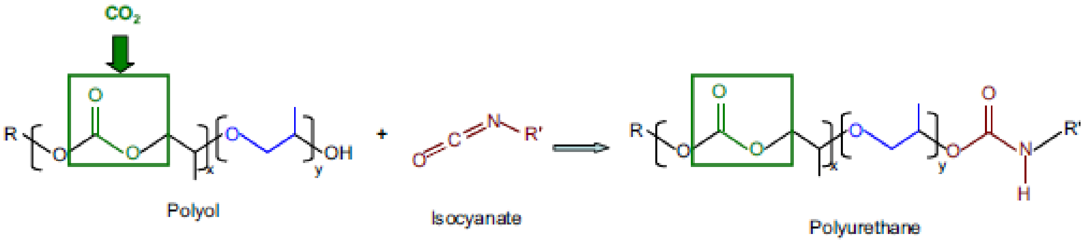
8.1.4.1.2 Polycarbonate polyols

Polyols are organic molecules containing multiple alcohol (-OH) groups in either primary or secondary positions. While a diversity of polyols exist in the market, polyether polyols, polyester polyols, and polycarbonate polyols constitute the majority of polyol production. Global consumption of all polyols is about 20 million t/y in 2014 and growing at around 6 % p.a., most of which is petroleum-based. Polyols are widely used in the polyurethane industry, and are important polymer additives for applications as plasticisers, chain extenders and processing aids (Muthuraj & Mekonnen 2018a).

An example of a representative polycarbonate polyol synthesis reaction is shown below. In this reaction, a polyethercarbonate polyol is synthesised by the polymerisation of propylene oxide (PO) with CO_2 using a double metal cyanide (DMC) catalyst and a multifunctional alcohol (e.g. glycerol) as starter (von der Assen & Bardow 2014).



Polyurethanes, with a global production of about 20 million tonnes in 2014 are among the top six most extensively used polymers. They are used in practically all fields of polymer applications – foams, elastomers, thermoplastics, thermorigids, adhesives, coatings, sealants, fibres, etc. (Muthuraj & Mekonnen 2018a). Polyurethanes are synthesised by the reaction of a polyol with an isocyanate:



The development of polycarbonate polyols with suitable functionality for use in polyurethane production is a topic of industrial significance, although it is currently at a fairly early stage of development. In general, a polyol of low functionality, having around 2-3 hydroxyl groups/mol and with a high molecular weight (MW) of 2000-10000 daltons, leads to an elastic polyurethane, while a low MW polyol of 300-1000 daltons, with a high functionality of around 3-8 hydroxyl groups/mol, leads to a rigid crosslinked polyurethane (Ionescu 2005). While much attention has been given to development of catalysts for high MW polycarbonates, much less has been given to the controlled synthesis of low MW CO_2/PO based polyols. A review of the relevant literature is provided by Qin et al. (2015).

A lifecycle assessment of polyethercarbonate polyol production found that incorporation of 20 wt.% CO_2 can reduce greenhouse gas emissions of polyurethane production by 11-19 %, and lower petrochemical usage by 13-16 % (von der Assen & Bardow 2014). As a further benefit, the hydrolysis/oxidation resistance of polyurethanes is improved through the use of CO_2-based polyols (Wang et al. 2016b).

The significant size and growth potential of the polyurethane market is motivating the industrial development of polycarbonate polyols that incorporate CO_2 as an alternative to petrochemical feedstocks.

8.1.4.1.2.1 Covestro

A leading role has been taken by Covestro (formerly Bayer Material Science), Germany, one of the world’s largest polymer companies, which has developed a range of polyether polyethercarbonate polyols called cardyon™. It is manufactured using multifunctional alcohol starters, which allow the production of polyols with a defined number ($2 \leq F \leq 4$) of terminal hydroxyl functions, enabling prospective applications in the preparation of foams, adhesives, coatings and fibres (Langanke et al. 2014).

In 2016, Covestro opened a 5,000 t/y production plant at Dormagen, near Cologne, shown in Figure 65 below. The CO_2 for the process is captured using a pilot amine absorption system at the RWE lignite power plant in Niederaußem (von der Assen & Bardow 2014).

Figure 65: *Covestro polyol production plant in Dormagen (© Covestro)*

The polyethercarbonate polyol, cardyon™, has been engineered initially for flexible polyurethane foam for use in mattresses and upholstered furniture, and is also being evaluated for use in the automotive industry (Langanke et al. 2014).

8.1.4.1.2.2 Novomer / Saudi Aramco

In the United States, Novomer has developed a catalyst system for production of a range of polypropylene carbonate (PPC) polyols, called Converge®, which contain more than 40 wt.% CO_2. Converge® PPC polyols are designed for use in polyurethane formulations targeted at adhesive, coatings, sealants, elastomers, and rigid and flexible foams. The manufacturing process uses waste CO_2 as a raw material, yielding a product with an extremely low carbon footprint and significantly lower cost than conventional petroleum-based raw materials. Manufacturing of Converge® PPC polyols is currently undertaken as a multi-thousand-ton commercial-scale toll facility in Houston, Texas.[127]

Converge® PPC polyols were introduced to the market in 2014, and in 2016 the technology and patent portfolio were sold to Saudi Aramco's subsidiaries, Aramco Services Company and Saudi Aramco Technologies, for up to US$100 million.[128]

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[127] https://sprayfoam.com/foam-news/novomer-announces-commercial-launch-of-converge-polyols-for-broad-use-in-polyurethanes-industry/2403

[128] https://polymer-additives.specialchem.com/news/industry-news/converge-polyols-novomer-saudi-aramco-000184483

8.1.4.1.2.3 Econic Technologies

Econic Technologies, based in Manchester, UK, has developed homogeneous Zn and Mg homogeneous catalysts for poly(cyclohexylene carbonate) (PCHC) production (Kember et al. 2009; Kember et al. 2012), as shown in Figure 66 below.

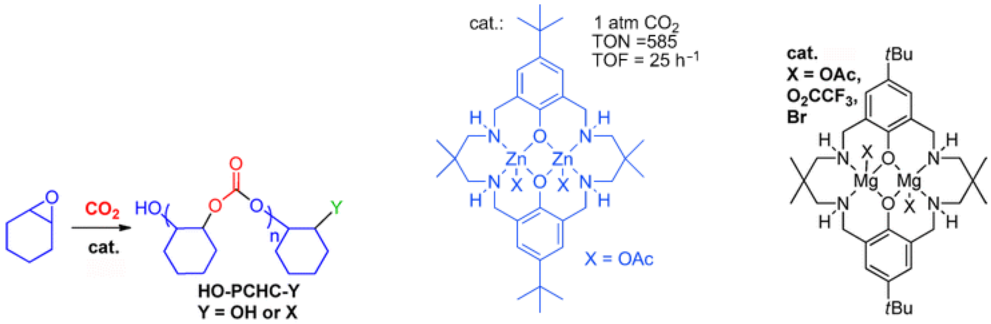

Figure 66: *Econic Zn and Mg catalysts for production of PCHC polyols (Kember et al. 2009; 2012)*

The tolerance of catalysts to impurities was demonstrated using CO_2 captured from the carbon capture demonstrator plant at Ferrybridge Power Station, U.K., is applied for the efficient production of PCHC. The catalysts showed high tolerance to amine, thiol, and water, without compromising catalytic activity/productivity or selectivity (Chapman et al. 2015).

In 2018, Econic Technologies opened a demonstration plant at a technical park in Runcorn, at The Heath. The demonstration plant will allow production of polyol samples under industrial conditions, to help encourage uptake by the industry.[129] In April 2022, Econic Technologies announced that it had closed the first round of a multimillion capital raise. The round was led by incoming investor, Capricorn Sustainable Chemistry Fund, with follow-on support from existing investor OGCI Climate Investments.[130]

8.1.4.1.2.4 Jiangsu Zhongke Jinlong-cas Chemical Co.

Jiangsu Zhongke Jinlong-cas Chemical Co., in Taixing, Jiangsu province, China, produces 50,000 t/y of biodegradable CO_2-polyols. The company produces poly (propylene carbonate) polyols by copolymerizing industrial waste gas CO_2 and epoxy propane in a loop reactor using a proprietary bimetallic catalyst (Chen & Huang 1996). The PPC polyols are used to manufacture film-grade thermoplastic elastomer TPU. It also produces CO_2-based flame-retardant insulation materials and waterborne polyurethane emulsion.[131]

8.1.4.1.2.5 Nantong Huasheng Plastic Products

Huasheng Polymer Co. has established a factory to produce 10,000 t/y of CO_2-polyols in Nantong, Jiangsu province (Liu & Wang 2017). It produces biodegradable PCO_2 bin liner bags, tee shirt bags

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[129] http://econic-technologies.com/news/uk-first-ccu-demo-plant/

[130] https://www.econic-technologies.com/econic-technologies-raises-funds-for-commercialisation-with-incoming-investor-capricorn-and-ogci-climate-investments/

[131] https://www.chemnet.com/Suppliers/36232/Jiangsu-Zhongke-Jinlong-cas.html

and agricultural mulch films which are exported to USA, Canada, Japan, Australia, New Zealand, etc.[132]

8.1.4.1.3 Non-isocyanate polyurethanes

Polyurethanes are usually synthesised by the reaction of a polyol with an isocyanate. In the previous section, it was shown that polyurethanes incorporating recycled CO_2 are being produced by reacting polycarbonate polyols with isocyanate. This is a net environmental benefit for polyurethane manufacture.

There is a great deal of interest in taking this further in the direction of environmental sustainability, by reducing the other fossil-derived ingredients used in the process. The key reactants, polyols and isocyanates, are fossil-derived and involve occupational health and safety risks. Polyols are usually produced using ethylene oxide or propylene oxide, which are hazardous and toxic compounds. Isocyanates are produced from toxic phosgene and are carcinogenic. Safer biological alternatives are being sought for both the polyol and isocyanate components, to produce bio-based non-isocyanate polyurethanes.

The most promising method to generate non-isocyanate polyurethanes (NIPUs) is the reaction between polycyclic organic carbonate oligomers and polyamines with primary amino groups, leading to the formation of poly(hydro urethane)s (PHUs) (Figovsky et al. 2013), as shown in Figure 67 below.

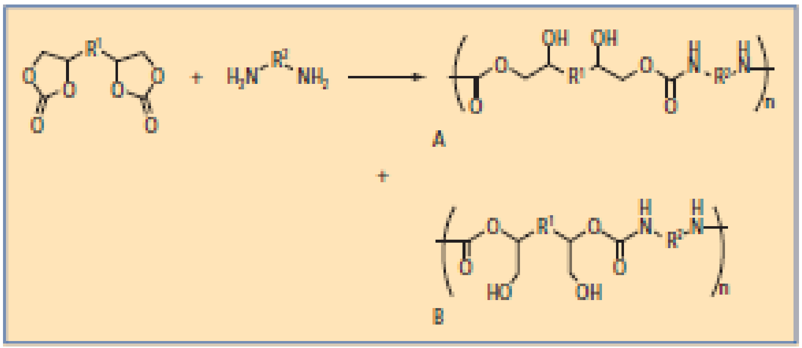

Figure 67: *β-hydroxyurethane moieties of NIPUs: A – with primary hydroxyl groups; B – with secondary hydroxyl groups (Figovsky et al. 2013)*

Bis-cyclic organic carbonates have been produced from plant seed oils, including sunflower, linseed and soybean oil. However, the flexible nature of vegetable oils often results in poor mechanical and thermal properties of the resulting PHU. The search for a more rigid molecular scaffold has led researchers to evaluate the use of lignin.

8.1.4.1.3.1 The use of lignin in non-isocyanate polyurethanes

Lignin is a polymeric component of woody plant tissue. The main source of lignin is the pulp and paper industry, where the Kraft process is predominantly used. A by-product stream of this process,

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[132] https://products.bpiworld.org/companies/nantong-huasheng-plastic-products-co-ltd

black liquor, typically contains 30-34 % lignin. In a conventional process, this stream is burned to provide energy for mill operations and to recover the cooking chemicals (Wallberg et al. 2006).

Early efforts to incorporate lignin into polyurethane synthesis typically followed one of two routes: (a) by direct utilisation of lignin without any preliminary modification, alone or in combination with other polyols, or (b) by making hydroxyl groups more readily accessible with the addition of extension groups via esterification and etherification reactions. This work has been reviewed previously (Borges da Silva 2009; Upton & Kasko 2015), and is summarised in Figure 68 below.

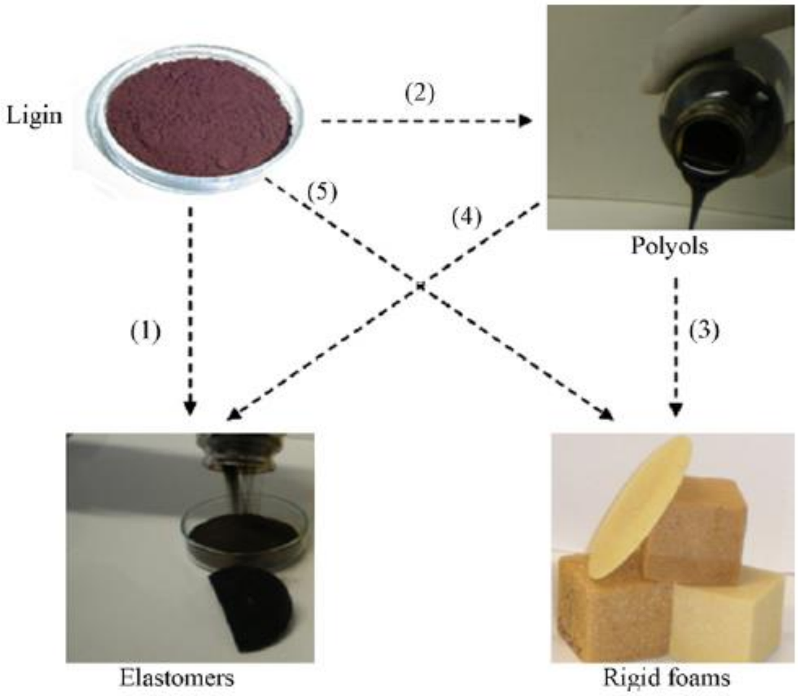

Figure 68: *Synthetic routes for lignin incorporation in polyurethanes: (1) direct use, (2) synthesis of liquid polyol, (3) synthesis of rigid polyurethane foams, (4) synthesis of polyurethane elastomers using lignin-based polyols, and (5) synthesis of rigid polyurethane foams using lignin as reactive filler (Borges da Silva et al 2009)*

Lignin polyols, suitable for use in isocyanate polyurethanes have been synthesised via oxyalkylation (Kühnel et al. 2015; Duval et al. 2017), and polycyclic carbonates have been synthesised from lignin for use in non-isocyanate polyurethanes (Salanti et al. 2017). However, while these methods are useful for improving the properties of polyurethane produced from lignin, they remain dependent on the use of toxic epichlorohydrin and propylene oxide.

Researchers at the University of Hamburg have reported the development of a novel, efficient and green protocol for synthesis of cyclic carbonate functionalised lignin for use in NIPUs (Kühnel et al. 2018). The procedure makes use of ethylene carbonate (EC), propylene carbonate (PC) and glycerol carbonate (GC), which are regarded as sustainable, nontoxic and environmentally friendly solvents and reagents.

The synthesis of cyclic carbonate functionalised lignin was completed in two steps, as shown in Figure 69 below. First, the lignin is oxyalkylated with GC, and then transesterified with either EC or DMC using K_2CO_3 as catalyst (Kühnel et al. 2018).

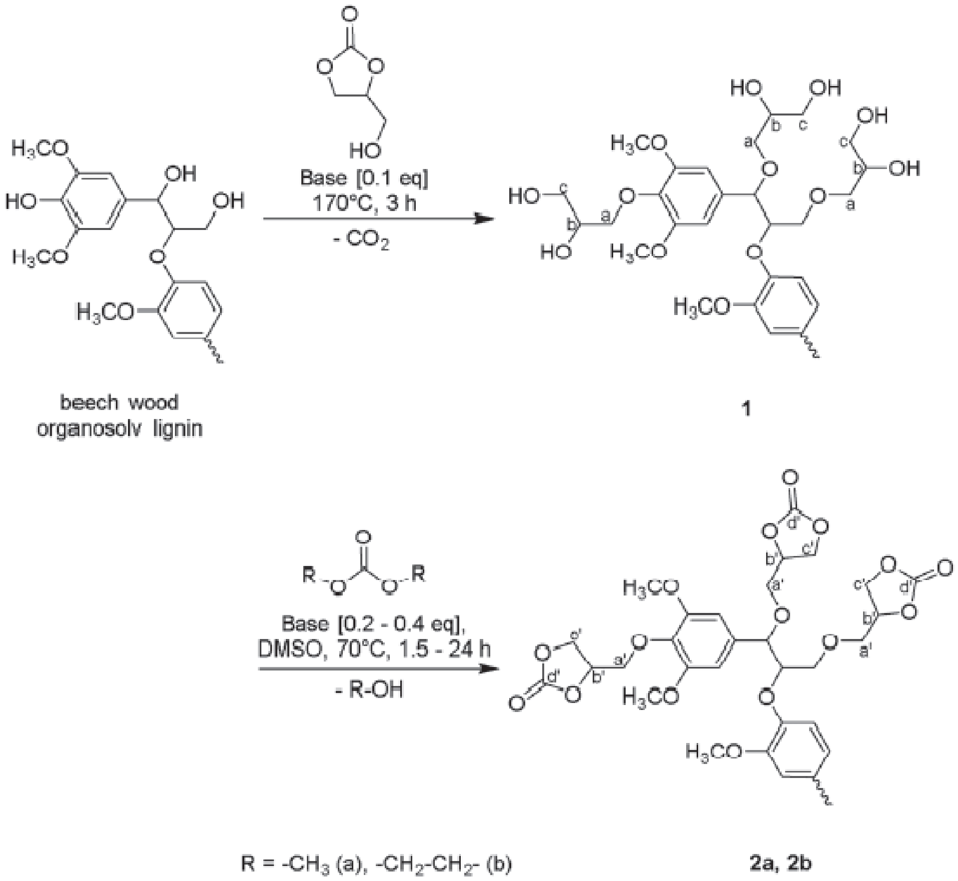

Figure 69: *Two-step synthesis involving oxyalkylation with glycerol carbonate, generating lignin terminated with 2,3-diol function (1), and transesterification with dimethyl carbonate or ethylene carbonate, to cyclic carbonate functionalised lignin (Kühnel et al. 2018)*

This procedure was completed within 6 hours at 75ºC and ambient pressure in the presence of catalytic amounts of K_2CO_3. Cyclic carbonate functionalised lignins were synthesised by transesterification with EC at 58-72% yield, while reaction with DMC resulted in 96% conversion (Kühnel et al. 2018).

This reaction scheme opens up the possibility of producing non-isocyanate polyurethanes in a safe, energy-efficient, environmentally friendly manner, using lignin waste from paper manufacture and organic carbonates made from recycled CO_2. This is a very significant development and worthy of further investigation and development.

8.1.4.2 Victorian Research Context

ACI is not aware of any relevant local research in this area.

8.1.4.3 ACI Comments

The chemistry of polycarbonate polymers and polyols is very versatile and represents a new and very important avenue for conversion of CO_2 into value-added products. The global carbonate market was valued at $3.5 billion in 2020, and is projected to reach $7.1 billion by 2030.[133] *The significant size and growth potential of the polyurethane market has motivated Covestro, Novomer and Econic Technologies to develop polycarbonate polyols incorporated recycled CO_2 for application in major consumer markets.*

At this stage, it does not seem likely that any Victorian company will seek to compete directly with these market leaders. However, there does appear to be an opportunity to become involved in the development of alternatives to the isocyanates used in polyurethane production, which are based on toxic precursors.

As explained above, researchers in Germany have recently developed a novel, efficient and green protocol for synthesis of cyclic carbonate functionalised lignin for use in non-isocyanate polyurethanes, making use of sustainable, nontoxic and environmentally friendly solvents and reagents (Kühnel et al. 2018). Waste lignin is produced in large quantities in the Latrobe Valley, at the Australian Paper papermaking plant at Maryvale. ***The possibility of combining waste lignin upgrading with CO_2 recycling, to produce a major commodity polymer in Victoria, is therefore of significant interest and potential.***

Support for the development of research expertise in this area, to enable further developments, seems to be warranted. An independent review of this topic is recommended, to help in the development of an appropriate research agenda to determine the extent of the opportunity and the investment required.

8.2 SYNTHESIS OF INTERMEDIATES AND FINE CHEMICALS

In the quest for 'greener' chemical synthesis routes, researchers worldwide are investigating opportunities for development of new processes using recycled CO_2 as a C1 carbon source. This is a relatively new field of research, which is only just starting to take off, and is applicable to a broad range of reactions. The main application for this class of chemistry is in the synthesis of reaction intermediates, but it is also applicable to the synthesis of bulk chemicals, e.g., urea, and fine chemicals, e.g., oxazolidinones.

This section provides a brief overview of this emerging area, to provide a glimpse into the broad range of possibilities that are being opened up for CO_2 recycling. The discussion that follows includes the utilisation of CO_2 for the synthesis of carboxylic acids, esters, carbamates, isocyanates, heterocyclic compounds and ureas.

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[133] Carbonate Market Statistics, Trends | Industry Analysis 2030 (alliedmarketresearch.com)

8.2.1 Carboxylic Acids (Acrylates) by Oxidative Coupling with Olefins

Acrylic acid, $CH_2{=}CHCO_2H$, is the simplest unsaturated carboxylic acid and is a building block for hundreds of consumer products. The global consumption of acrylic acid is estimated to reach 8.2 Mt/y by 2020, with a market value of US$18.8 billion. The primary use of acrylic acid is in the production of acrylic esters and resins, which are used primarily in coatings and adhesives. It is also used in oil treatment chemicals, detergent intermediates and water treatment chemicals. Sodium acrylate is a key basic intermediate for the large market of polyacrylates (>25 Mt/y), which are used as super-absorbents in diapers (Aresta et al. 2016).

Traditionally, acrylates have been synthesized exclusively via a two-step oxidation of propene with O_2 over heterogeneous catalysts at high temperature. An alternative route, involving the synthesis of acrylic acid by direct combination of CO_2 with ethene, has been actively investigated as a “dream reaction” for over 4 decades:

$$CH_2{=}CH_2 + CO_2 \rightarrow CH_2{=}CHCO_2H$$

The range of catalytic reaction schemes that have been developed have previously been reviewed (Liu et al. 2015; Wang et al. 2017a). To date, the most efficient system achieved has been developed by BASF, in conjunction with Heidelberg University. The current best process uses a palladium-based complex, $Pd(PPh_3)_4$ (where PPh_3 = triphenylphosphine), in combination with 1,2-bis(dicyclohexylphosphino) ethane (dcpe) as the catalysts and sodium isopropoxide (NaOiPr) as a regenerable alkoxide base. The reaction is conducted in the solvents *N,N*-dibutylformamide (DBF) or *N*-cyclohexylpyrrolidone (CHP), which have limited miscibility with water (Manzini et al. 2017). The reaction scheme is shown in Figure 70 below.

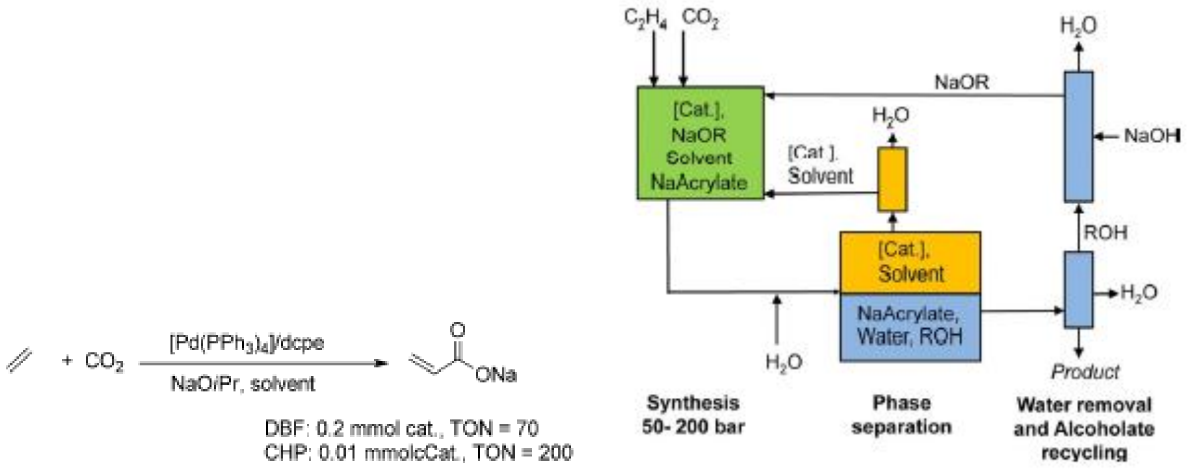


Figure 70: *Process concept for the Pd-catalysed synthesis of sodium acrylate from ethylene and CO_2 using amide solvents and NaOiPr (Manzini et al. 2017).*

The reaction is performed in a reactor that contains the organic solvent, the base, the catalyst, ethylene and CO_2. Reaction conditions are: 10 bar ethylene, 40 bar CO_2, 20 h, 145 ^{o}C. To separate the sodium acrylate from the catalyst, water is added to a continuous stream from the reactor after de-pressurisation. The alcohol formed in the reaction is distilled off from the product phase and recycled with NaOH to leave the pure sodium acrylate behind. The catalyst in the organic solvent is be recycled back into the reaction after phase separation, with evaporation of water to prevent loss of catalyst activity (Manzini et al. 2017). Current research efforts are focused on the development of a lab-scale continuous rig for demonstrating proof-of-concept of sodium acrylate synthesis from ethylene and CO_2.

Beyond acrylic acid, there is a wide range of more complex unsaturated carboxylic acids that are of commercial interest. Currently, the formation of a terminal carboxylic moiety, $C\text{-}CO_2$, is achieved industrially through a variety of routes, such as oxidation of hydrocarbons or aldehydes, dehydrogenation of alcohols, carbonylation reactions, oxidative cleavage of olefins, etc. None of these routes is ideal, being poorly selective or not quantitative, producing waste and a loss of carbon (Aresta et al. 2016).

Alternatively, a terminal carboxylic moiety can be introduced by catalytic coupling of CO_2 with unsaturated substrates such as olefins, alkynes, allenes and conjugated dienes. Currently, such reactions are employed on a small scale for the synthesis of high value chemicals, as has recently been reviewed (Aresta et al. 2016; Yan et al. 2018).

8.2.2 Carboxylic Acids by CO_2 Incorporation Into C-H Bonds

The direct C-H carboxylation with CO_2 provides another potential route to carboxylic acids:

$$R\text{-}H + CO_2 \rightarrow R\text{-}CO_2H$$

Currently, the only industrial exploitation of this reaction is the Kolbe-Schmitt reaction for production of salicylic acid. In this reaction, phenol sodium salt reacts with carbon dioxide to produce an *ortho*-derivative, as shown in Figure 71 below.

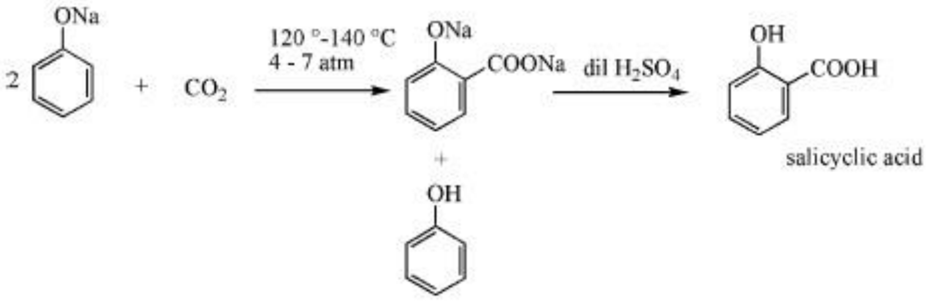
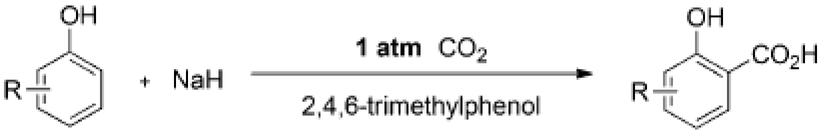


Figure 71: *Kolbe-Schmitt reaction for production of salicylic acid (Omae 2012)*

The Kolbe-Schmitt reaction was developed in 1860 by Kolbe, and the yield was improved under reaction conditions at 125 ^oC and 4-7 atm CO_2 pressure by Schmitt in 1885. Salicylic acids are important motifs in pharmaceuticals and agrochemicals and are important intermediates in organic synthesis. Currently, about 16,000 t/y of acetylsalicylic acid (aspirin) is produced via this route (Omae 2012).

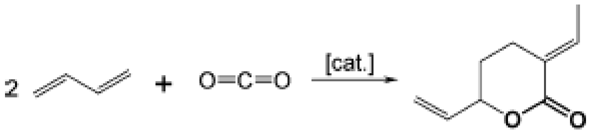
While the Kolbe-Schmitt process is widely used in industry, it is difficult to implement at laboratory scale, as it involves high temperatures and pressures, and two separation stages. Development of alternative routes to carboxylic acids by catalytic carboxylation of C-H bonds has been a challenging research area (Aresta et al. 2016). Recently, however, researchers at the University of Manchester reported a new method for carbonylation of phenols with CO_2 at atmospheric pressure (Luo et al. 2016). The reaction uses sodium hydride (NaH) as a base, and is conducted in the presence of 2,4,6-trimethylphenol to increase CO_2 absorption:



This process has been successfully used to prepare a broad variety of salicyclic acids (Luo et al. 2016).

8.2.3 Esters from Unsaturated Hydrocarbons

Under suitable conditions, CO_2 and unsaturated organic substrates (alkynes, allenes, conjugated dienes and others) can be catalytically reacted to produce industrially useful compounds such as linear and cyclic esters. The most advanced example in this category is the synthesis of δ-lactone from 1,3-butadiene and CO_2 using a homogeneous palladium catalyst system:



This reaction has been optimised and developed to the laboratory miniplant scale, with a selectivity for δ-lactone of 95 % and 45 % conversion of butadiene achieved by recycling by-products (Behr & Becker 2006). It proved possible to close all solvent and catalysts loops, as shown in Figure 72 below, yielding a stable process suitable for industrial scale up (Behr & Henze 2011).

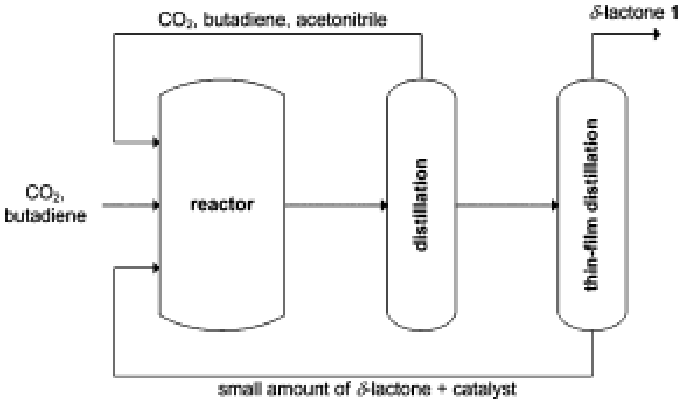


Figure 72: *Flow scheme for the production of δ-lactone (Behr & Henze 2011)*

The resulting δ-lactone is a highly functionalised compound that can be further synthesised into a wide range of products, including carboxylic acids, alcohols and diols, aldehydes, esters, silanes, epoxides and polymers (Behr & Henze 2011).

It was subsequently reported that an improved catalyst system afforded a remarkably high turnover number of 4500 with a selectivity for δ-lactone of 96 % after 5 h reaction at 70 ^{o}C (Balbino et al. 2018). However, there has not yet been any report of the process being scaled up further.

8.2.4 Carbamates

One of the most promising fields for CO_2 utilisation is the synthesis of carbamates. Carbamates comprise one of the most important classes of organic compounds found in natural products, pharmaceutically active compounds and agrochemicals (pesticides, herbicides, insecticides, fungicides, etc.). In organic chemistry, carbamates are used as precursors in the synthesis of isocyanates and ureas. Current commercial processes for production of carbamates include alcoholysis of isocyanates and aminolysis of chloroformates, both of which are based on the use of highly toxic and corrosive phosgene ($COCl_2$) (Aresta et al. 2016).

The use of CO_2 in carbamate synthesis is particularly attractive since CO_2 is a non-toxic, non-corrosive, inflammable, abundant and cheap C1 source. Despite its stability, it easily combines with amines at ambient temperature and atmospheric pressure to form the corresponding carbamic acids:

$$RNH_2 + CO_2 \xrightarrow[\text{base}]{} RNHCOOH$$

This chemistry is currently utilised in CO_2 capture technologies, where amines such as MEA and MDEA are employed to remove CO_2 from industrial exhaust gases.

Carbamic acids can then be reacted with alcohols, halides or diazomethanes to produce carbamate esters, which are used in pharmacology and agrochemistry. However, this reaction is difficult to achieve in good yields because it is subject to formation of undesired alkylated amines as side-products. As a result, only a relatively small number of useful chemical products have been developed using this route (Omae 2012; Aresta et al. 2016).

A more attractive route is the one-pot synthesis of carbamates from amines, CO_2 and alcohols, in which water is the only reaction co-product:

$$RNH_2 + CO_2 + R'OH \rightleftharpoons RNHCO_2R' + H_2O$$

This represents an environmentally friendly route to carbamates, although the presence of co-produced water is a complication.

Ion et al. (2008) demonstrated that carbamates can be synthesised from CO_2, amines and alcohols using a series of inexpensive and readily available basic catalysts in good yield under mild reaction conditions, even in the absence of dehydrating agents. Similarly, Honda et al. (2011) showed that cerium oxide can be used as a catalyst for carbamate synthesis in the absence of dehydrating agents. To date, however, such processes have not yet progressed beyond lab scale.

An alternative route for synthesis of carbamates, from CO_2, amines and epoxides is also an area of active research internationally. A recent review of this topic found that the successes to date have been accomplished at high temperatures and predominantly use aromatic amines. More work is needed to develop catalytic systems capable of producing carbamates from CO_2 and aliphatic amines using epoxides under mild conditions (Hosseinian et al. 2018).

8.2.5 Isocyanates

As described in Section 8.1.4.1.2 above, polyurethane polymers are synthesised by the reaction of a polyol with an isocyanate, R-NCO. As explained there, companies such as Covestro and Novomer are developing new polyol polymers that incorporate CO_2 as an alternative to petrochemical feedstocks.

The global market for isocyanates is around 11 Mt/y, valued at US$38 billion (Aresta et al. 2016). All isocyantes are currently produced using toxic phosgene, so it is desirable to develop more environmentally friendly alternatives.

In principle, isocyanates can be directly synthesised from amines and CO_2:

$$RNH_2 + CO_2 \rightleftharpoons RNCO + H_2O$$

Researchers at Monsanto have patented a method that allows this reaction to proceed quickly, with high yield under mild conditions, using a tertiary organic co-base in the presence of dehydrating agents (McGhee et al. 1995). However, the use of large quantities of co-base and the production of large quantities of waste makes the exploitation of this process on a large industrial scale difficult (Aresta et al 2016).

Currently, a new approach to synthesis of isocyanates from CO_2 is being developed in the Carbon2Polymers project, which is an EU-funded collaboration between RWTH Aachen University, CAT Catalytic Center Aachen, Forschungszentrum Jülich and Covestro. The goal of the Carbon2Polymers project is ultimately to produce isocyanates using CO_2 captured from steel mill gas and hydrogen produced by electrolysis. The proposed reaction sequence comprises the hydrogenation of captured CO_2 and subsequent esterification to methyl formate (MF). MF is converted to toluene 2,4-dicarbamate (TDC) in an oxidative carbonylation step. Subsequently, TDC is cleaved into toluene-2,4-diisocyanate and methanol (Kaiser et al. 2018). The steps of this sequence have been studied individually, and current research efforts are focused on unifying the reaction sequence into a single viable process (Leitner et al. 2018).

8.2.6 Heterocyclic Compounds

Heterocyclic compounds are cyclic structures that comprise rings with atoms of at least two different elements. They are widely found in nature and represent an important class of building blocks for the synthesis of medicinal compounds. In recent years, a wealth of CO_2 incorporation reactions for heterocycles synthesis have been disclosed. As illustrated in Figure 73 below, these can be roughly divided into four categories (Yu & He 2015):

1. cycloaddition of high-energy starting materials such as three- or four-membered ring compounds with CO_2 to cyclic carbonates or oxazinanones;
2. cascade sequence involving the benzyne species generated in situ from *o*-trimethylsilylphenyl triflate via 1,2-elimination, addition reaction with an imine and CO_2, followed by intramolecular cyclization of the carboxylate intermediate;
3. intramolecular cyclisation of an isocyanate intermediate through dehydration of the carbamic acid from a diamine substrate and CO_2; and
4. intramolecular nucleophilic ring-closing reaction of a carboxylate intermediate via addition of CO_2 to a nucleophilic site generated *in situ*.

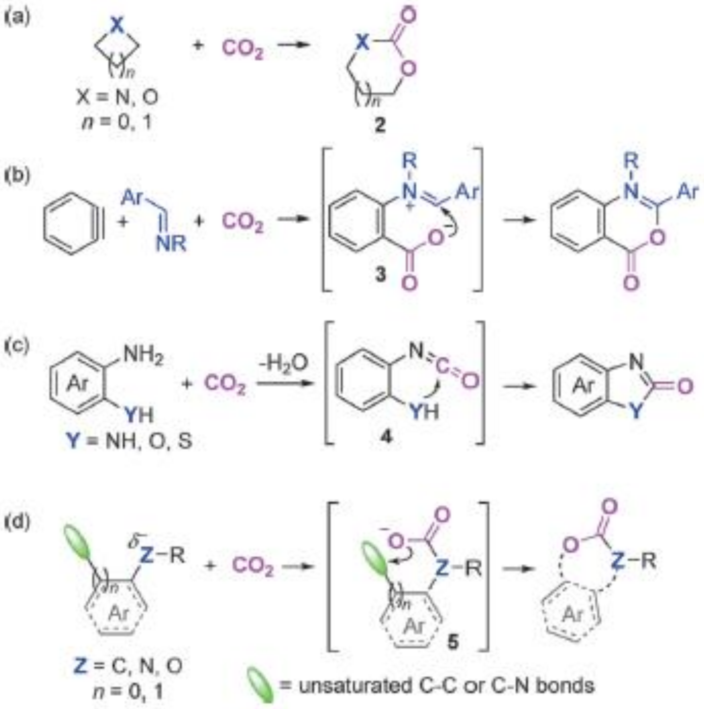
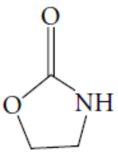


Figure 73: *Summary of reaction schemes for synthesis of heterocycles using* CO_2 *(Yu & He 2015)*

This is an area of active international research interest, although still at the laboratory proof-of-concept stage. Detailed reviews of these investigations are available elsewhere (Yu & He 2015; Didehban et al. 2018).

One particular class of heterocyclic compounds of interest are the oxazolidinones, containing 2-oxazolidine in the structure, i.e., where the carbon between the nitrogen and oxygen is oxidized to a ketone:



Oxazolidinones have applications in pharmaceuticals as antibiotics and anticancer agents, and in agricultural herbicides. They are also used in the paint and varnish industry, in polymer synthesis to prepare foams with high thermal stability, and also as solvents in lithium-ion batteries and in ink-jet printing (Pulla et al. 2013). There are many reported methods to synthesise 2-oxazolidinone derivatives, but the high cost and/or toxicity of the reagents involved does not allow their preparation to be extended to large-scale production (Farshbaf et al. 2018). However, oxazolidinones are viewed as a promising class of fine chemicals that may be a good target for synthesis using recycled CO_2 (Otto et al. 2015).

Three main strategies have been developed for synthesising oxazolidinones using CO_2: (i) reaction of aziridines with CO_2; (ii) reaction of propargylamines with CO_2, and (iii) reaction of 2-amino alcohols with CO_2. Of these, 2-amino alcohols appear to offer greatest promise, as they are simple, easily available and economic substrates (Pulla et al. 2013). However, most of the reaction schemes to date involve organic solvents, which have serious environment and safety concerns. While some solvent-free systems have been developed, they high temperatures and/or pressures. Further catalyst development is needed to allow more efficient synthesis of oxazolidinones using CO_2 under milder conditions (Arshadi et al. 2019).

8.2.7 Ureas

Ureas are a class of organic compounds with the formula $(R_2N)_2CO$ where R = H, alkyl, aryl, etc. Ureas are bioactive compounds that are found widely in natural products, agricultural pesticides, herbicides and pharmaceuticals. The simplest of the ureas, called urea, $(NH_2)_2CO$, comprises two $-NH_2$ groups joined by a carbonyl (C=O) functional group.

Globally, production of urea in 2023 was 188 million tonnes, and is forecast to expand at ~1.5% annually to 206 million tonnes by 2028.[134] The demand for urea is predominantly driven by its use as a fertiliser, but also for conversion to melamine and melamine-urea-formaldehyde resins for manufacture of particleboards (Jarvis & Samsatli 2018).

8.2.7.1 Urea manufacture

Urea is produced commercially by reacting CO_2 with ammonia at elevated temperature and pressure, typically 185 ^{o}C and 150 bar, with overall conversion of CO_2 in the region of 85-90% (Pérez-Fortes et al. 2014). The process consists of two main equilibrium reactions, with incomplete conversion of the reactants. The first is carbamate formation: the fast exothermic reaction of liquid ammonia with gaseous CO_2 at high temperature and pressure to form ammonium carbamate:

$$2\ NH_3 + CO_2 \rightleftharpoons H_2N\text{-}COONH_4$$

The second is urea conversion: the slower endothermic decomposition of ammonium carbamate into urea and water:

$$H_2N\text{-}COONH_4 \rightleftharpoons (NH_2)_2CO + H_2O$$

These reactions are not compatible, with the high temperature required for the first being unfavourable for complete conversion in the second. To maximise the efficiency of the process, a complex ‘stripping process’ has been developed, representing the current state of the art (see Figure 74 below).

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[134] https://www.mordorintelligence.com/industry-reports/industrial-grade-urea-market

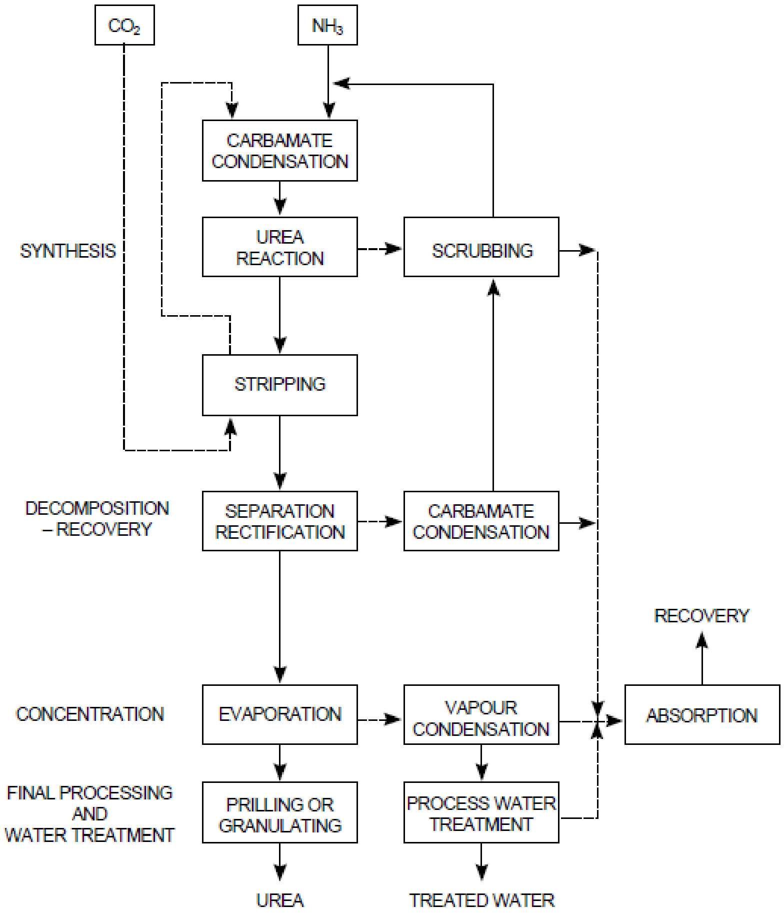

Figure 74: *Block diagram of a total recycle NH_3 stripping urea process (EFMA 2000)*

Commercial urea plants are usually connected to ammonia synthesizing plants, in which hydrogen is generated by steam reforming of natural gas. This produces CO_2 as a relatively pure by-product, but there is not enough to convert all of the ammonia to urea. Hence, the size of the urea plant is constrained by the upstream ammonia facility. If the price of urea is higher relative to ammonia, there is an incentive to convert the surplus of ammonia into urea using CO_2 recovered from other sources (Pérez-Fortes et al. 2014).

This presents an opportunity for urea manufacturers to increase output by utilising CO_2 captured from a related process. One of the first examples of this was undertaken by Gulf Petrochemical Industries Company (GPIC), located at Sitra in the Kingdom of Bahrain. In this project, which was commissioned in 2009, CO_2 is captured from a methanol plant and used for complete conversion of ammonia at a urea plant nearby.[135] The process technology employed at this plant was jointly developed by Mitsubishi Heavy Industries and Kansai Electric Power Company (Zangeneh et al. 2011).

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[135] http://www.gpic.com/responcibility/CDRmoved/

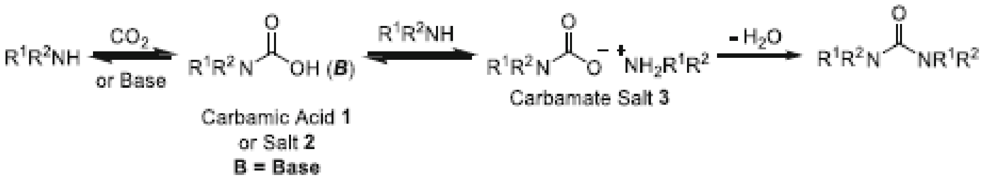
In Saudi Arabia, United Jubail Petrochemical Company (UNITED), a manufacturing affiliate of the Saudi Basic Industries Corporation (SABIC), commissioned the world's largest CO_2 purification plant in 2015. The facility, designed and built by Linde, captures and purifies up to 500,000 Mt/y of CO_2 from an ethylene glycol plant. It is then channelled through a network to other SABIC affiliates, where it is used in the production of useful products, including urea, food-grade CO_2 for the food and drink industry, and methanol.[136]

Urea production and yield boosting with CO_2 is currently a mature and widely implemented technology, with a TRL of 9.

8.2.7.2 Dialkylureas

At a much smaller scale, *N,N′*-dialkylureas are very important raw materials and/or intermediates in the production of fine chemicals, such as pesticides, herbicides, pharmaceuticals, polyurethanes, and plant growth regulators. They are also used as dyes for cellulose fibre, antioxidants in petrol, and corrosion inhibitors. Currently, the commercial production of *N,N′*-dialkylureas involves the highly toxic phosgene as a starting raw material, which generates corrosive HCl as a byproduct (Aresta et al. 2016).

The search for efficient methods for synthesis of ureas using CO_2 has been of long-standing industrial interest. The general process for producing ureas is shown below (Wang et al. 2017b):



The reaction of CO_2 with amines to produce carbamate proceeds readily at room temperature and low CO_2 pressure. Under catalytic conditions, the carbamate is dehydrated to generate urea, with the removal of H_2O. However, each of these reactions is reversible, so the efficient conversion of carbamic acids or carbamate anions into ureas remains an ongoing challenge (Wang et al. 2017b).

A wide range of synthesis routes for production of ureas have been developed and have recently been reviewed. It was shown that many different types of catalysts are effective for activation of CO_2, amine, or carbamate intermediates. However, the efficient removal of water is the key factor and often (over)stoichiometric amounts of dehydrants are required, thereby generating large volumes of waste. This suggests that further process improvements are needed for cost-effective production of ureas using CO_2 (Wang et al. 2017b).

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[136] https://www.sabic.com/en/news/4055-sabic-highlights-innovation-with-details-of-world-s-largest-co2-purification-plant-in-sustainability-report

8.2.8 Victorian Research Context

Latrobe Hydrogen (formerly Latrobe Fertilisers) is currently working toward establishing a urea production plant in Victoria, as a replacement for urea imported from overseas.

The other reaction routes described in the foregoing section are predominantly used as intermediate steps in the synthesis of bulk and fine chemical. It is currently unknown whether they are relevant to any of the chemical companies based in Victoria.

8.2.9 ACI Comments

It was stated above (Section 8.2.7.1) that the amount of CO_2 *produced during production of ammonia is not enough to allow all of the ammonia to be converted to urea. This needs to be qualified. Commercial synthesis of ammonia involves production of hydrogen by (i) generation of syngas by either steam reforming of natural gas or gasification of coal, and (ii) conversion of CO to* H_2 *and* CO_2 *by the water-gas shift reaction. It is indeed correct to say that the amount of* CO_2 *released during hydrogen production is insufficient for conversion of all the ammonia to urea. However, the steam reforming, gasification, and water-gas shift reactions are all endothermic, and require input of additional energy to maintain the high temperatures involved. This energy is conventionally generated by combustion of fossil fuel, creating additional* CO_2 *which is typically not captured. Values for total* CO_2 *emissions associated with ammonia synthesis are absent from the literature, although it is generally understood that the quantities involved (if captured – which they currently aren't) would significantly exceed the amount required for urea production.*

In the Victorian context, the proposed HESC process is expected to produce 225,000 t/y hydrogen and 4.39 Mt/y CO_2 *by-product (Kamiya et al. 2015). This amount of hydrogen could be converted to 1.56 Mt/y ammonia and then 2.7 Mt/y urea, consuming 1.8 Mt/y* CO_2 *in the process. Thus, producing ammonia from Victorian lignite would generate more* CO_2 *than needed for urea synthesis. In this case,* ***urea synthesis would consume about 41% of the waste*** CO_2***, representing a major*** CO_2 ***recycling opportunity.***

Currently, Australia imports about 2.4 million t/y of urea, around 90 % of domestic demand. In April 2023, construction began on the $6 billion Perdaman urea project near Karratha WA, which will produce 2.3 million t/y urea from natural gas from mid-2027. Incitec Pivot has already signed a 20-year deal with Perdaman to take up to 2.3 million t/y, of which up to 50% will be marketed within Australia and the remainder exported to key destinations.[137]

There is thus a strong argument to be made for at least one additional facility in the Latrobe Valley to convert lignite into blue ammonia and/or urea for both the domestic and export markets. As is done elsewhere, the balance of production could be shifted between ammonia and urea in response to market demand and relative prices, to maximise the profitability of the operation. This would create significant new employment opportunities in the Latrobe Valley and boost the Victorian economy.

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[137] https://www.abc.net.au/news/2023-04-29/falling-urea-prices-a-win-for-famers-and-shoppers/102276888

This will also ***create an opportunity for conversion of CO_2 and hydrogen into bulk and fine chemicals****, extending the hub concept to low-emissions chemicals manufacture. It is evident that the development of new chemical synthesis routes to allow the use of recycled CO_2 is a new and very active area of international research. It is very early days, but it seems certain that this will prove to be a profitable field of investigation.* ***ACI recommends that an independent review of developments in this area be undertaken by a qualified expert, to provide guidance on the opportunities that exist for strategic research efforts. This review should include detailed consultations with representatives of the relevant chemicals and plastics industries.***

8.3 CATALYTIC REDUCTION OF CO_2

This section describes processes in which CO_2 is reduced to a lower oxidation state by a reaction involving hydrogen. These processes can make some of the most valuable products from CO_2 recycling, including formic acid, methanol, carbon monoxide, syngas, olefins and fuels. The key to these processes is the development of efficient catalyst and reaction systems to allow operation under mild conditions of temperature and pressure.

The processes described in this section are dependent on the availability of low-cost CO_2-free hydrogen. Each process will have its own optimum scale of operation for commercial viability, and this is likely to influence the selection of an appropriate hydrogen source (e.g., from electrolysis or gasification). It is beyond the scope of this report to consider all the various scenarios that may be possible.

8.3.1 Formic Acid

Formic acid, HCOOH, is a valuable basic chemical with a concentrated, small and mature market of about 760 kt/y (Pérez-Fortes et al. 2016). This has been subsequently reviewed and the the global formic acid market size was valued at USD 1.86 billion in 2022 and is projected to grow at a CAGR of 9.53% from 2023 to 2030[138]. It is used in textiles (leather and tanning), pharmaceuticals and food chemicals, due to its strong acidic nature and reducing properties. As an industrial chemistry intermediate compound, formic acid plays a major role as an acid, a reductant and a precursor for syntheses (Gunasekar et al. 2016).

There is currently a great deal of research interest in formic acid as both an energy source and energy carrier. Formic acid has emerged as a promising fuel source in direct liquid fuel cell systems due to its excellent oxidation kinetics, high cell potential and fewer fuel crossover problems (Uhm et al. 2009). As a potential hydrogen carrier, formic acid has a relatively low H_2 content (4.4 wt%) but is environmentally benign and is easy to store and transport (Jiang et al. 2010).

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[138] https://www.marketresearchfuture.com/reports/formic-acid-market-1132

Formic acid is produced industrially by combining carbon monoxide and methanol in strong base to produce methyl formate, which is then hydrolysed in the presence of an excess of water to methanol and formic acid.

$$CH_3OH + CO \xrightleftharpoons{\text{NaOMe (cat.)}} HCO_2CH_3$$

$$HCO_2CH_3 + H_2O \rightleftharpoons HCO_2H + CH_3OH$$

Downstream processing is tedious, as formic acid forms a high-boiling azeotrope with water (Klankermayer et al. 2016). This process produces about 3 tonnes of CO_2 per tonne of formic acid. In contrast, the emission of CO_2 could be reduced to 100kg/t by synthesising formic acid from CO_2 (Gunasekar et al. 2016).

In principle, the hydrogenation of CO_2 to formic acid is a simple reaction:

$$CO_2 + H_2 \rightleftharpoons HCOOH$$

However, the thermodynamics of this reaction are unfavourable, so the conversion is typically increased by using a product stabiliser to improve the thermodynamics (Kaiser et al. 2018):

$$CO_2 + H_2 \rightleftharpoons HCOOH$$

$$HCOOH + x\text{Stab.} \rightleftharpoons [HCOOH/x\text{Stab.}]$$

This approach was first used by Royal Dutch Shell, making use of secondary amines (e.g. $HNMe_2$) as stabilisers during hydrogenation (Haynes et al. 1970). Since then, highly efficient catalysts have been developed for hydrogenation of CO_2 to formate, both homogeneous and heterogeneous. Reviews of catalyst development are available and not discussed further here (Wang et al. 2011; Gunasekar et al. 2016; Klankermayer et al. 2016; Dabral & Schaub 2019).

Recovery of the formic acid produced in the hydrogenation reaction is a significant challenge. Separation of formic acid from the (typically) homogeneous catalyst by distillation is not feasible because it shifts the equilibrium back to CO_2 and H_2, resulting in decomposition of the formic acid (Leitner et al. 2018). To overcome this intrinsic problem, biphasic catalysis has been developed, to obtain a catalyst-free product phase which can be further processed to isolate formic acid.

8.3.1.1 BP process

The first biphasic system was patented in BP (Green et al. 1989), as illustrated in Figure 75 below.

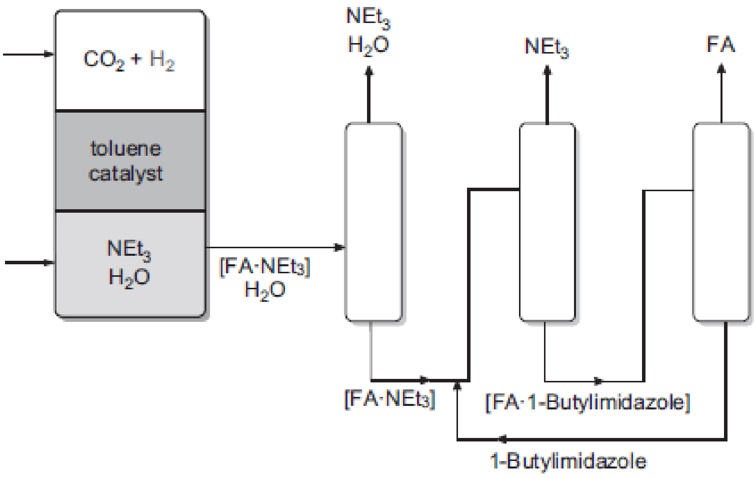

Figure 75: *BP process for hydrogenation of CO_2 to formic acid (FA) (Leitner et al. 2018)*

The BP process included water as the product phase and toluene as the catalyst phase. The catalyst was $[RuCl_2(PPh_3)_2]$ (where PPh_3=triphenylphosphine), with triethylamine (NEt_3) as stabilizing agent. After water removal and separation of the $[FA·NEt_3]$ adduct, no direct isolation (e.g., by thermal cleavage) of the formic acid from this mixture was possible, as $[FA·NEt_3]$ forms a stable azeotrope. To isolate formic acid, the adduct was mixed with an excess of 1-butyl-imidazole resulting in the liberation of NEt_3, which could be separated as a low boiling amine. Subsequently, the [FA·1-butylimidazol] adduct was cleaved at 180 °C to obtain pure formic acid (Leitner et al. 2018).

8.3.1.2 BASF process

More recently, BASF developed a water-free system comprising trihexylamine ($NHex_3$) as the catalyst phase in combination with the metal complex $[\{RuCl_2(COD)\}_2]$ and the phosphine ligand P^nBu_3 (Schaub et al. 2013), shown in Figure 76 below. For the product phase, the polar high boiling diol 2-methyl-1,3-propandiol was used.

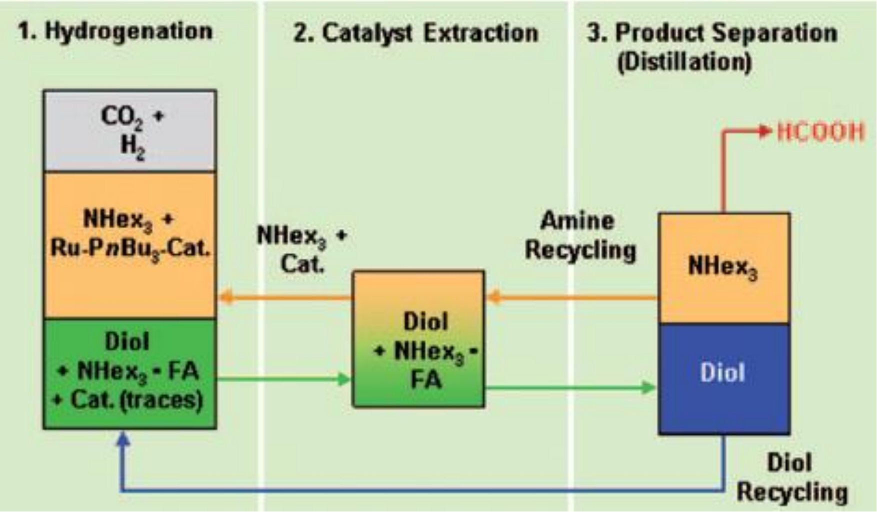

Figure 76: *Production of formic acid by CO_2 hydrogenation in amine (Schaub & Paciello 2011)*

This process was based on the key observation that [FA·Hex3] salts are not miscible with the free amine and can be cleaved thermally to give pure formic acid and the amine under relatively mild conditions (150 °C, 150 mbar) (Schaub & Paciello 2011). However, after phase separation it was found that non-negligible amounts of catalyst were found in the product phase, which had to be removed before thermal cleavage of [FA·Hex3] could be accomplished, rendering the process more complex. BASF scaled this process up to pilot plant level but has not yet proceeded with commercialisation (Lietner et al. 2018).

8.3.1.3 Carbon2Polymers process

Currently, a new variation on this theme is being developed by the Carbon2Polymers project, which is an EU-funded collaboration between RWTH Aachen University, CAT Catalytic Center Aachen, Forschungszentrum Jülich and Covestro. The goal of the Carbon2Polymers project is ultimately to produce isocyanates using CO_2 captured from steel mill gas and hydrogen produced by electrolysis. The first step in the process is to produce formic acid by hydrogenation of CO_2 (Kaiser et al. 2018). This is accomplished using a biphasic catalytic system, illustrated in Figure 77 below, similar to the strategy developed by BP.

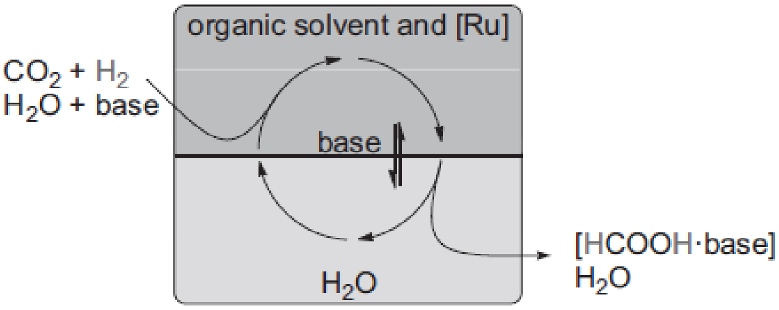

Figure 77: *Carbon2Polymers biphasic strategy for formic acid synthesis (Leitner et al. 2018)*

The reaction system consists of an organic liquid phase (methylisobutylcarbinol, MIBC) containing a homogeneous *cis*-$[RuCl_2dppm_2]$ catalyst. The amine stabiliser is methyl diethanolamine (MDEA), which is used at industrial scale for CO_2 scrubbing. An automated laboratory-scale system has been constructed and used to demonstrate effective hydrogenation of CO_2 in a saturated aqueous MDEA feed, mimicking a real scrubbing solution. High efficiency and stability were maintained over 11 cycles (Leitner et al. 2018).

Researchers from BASF have pointed out that the disadvantage of the biphasic production route is that the driving force for the CO_2-hydrogenation is provided by the formation of the formic acid-amine salts. Therefore, at least the same energy input has to be provided during the distillation step to cleave these salts, leading to a significant cost impost when compared to the state-of-the art route based on CO. The overall reaction thermodynamics using CO instead of CO_2 are far more favourable, so there is merit in considering the use of a reverse water-gas shift reaction to generate CO from recycled CO_2 (Dabral & Schaub 2019):

$$CO_2\ (g) + H_2\ (g) \rightleftharpoons CO\ (g) + H_2O\ (l)$$

In order to improve the economics of producing formic acid by hydrogenation of CO_2, improved catalyst systems are needed. It remains necessary to develop a catalyst system based on inexpensive transition metals exhibiting high stability over repeated recycles (Gunasekar et al. 2016).

8.3.1.4 Victorian Research Context

ACI is unaware of any research being undertaken in Victoria on catalytic synthesis of formic acid.

8.3.1.5 ACI Comments

Formic acid is an important industrial chemical and synthesis reaction intermediate. However, there are serious challenges involved in overcoming the thermodynamic barriers to the catalytic reaction and driving the reaction toward completion. Given the lack of an existing research base in this area, ACI does not recommend initiation of research on this topic in Victoria.

8.3.2 Formaldehyde

Formaldehyde, HCHO, is an important bulk chemical that is used in the synthesis of disinfectants, pharmaceuticals, paints, inks, cosmetics, resins, polymers and adhesives, with an annual global production of over 30 Mt/y (Heim et al. 2017). Formaldehyde is currently produced industrially by the catalytic oxidation of methanol, which is a highly exothermic reaction. In the commonly used Formox process, methanol is oxidised in the presence of excess air and a modified iron-molybdenum-vanadium oxide catalyst at 250-400ºC (Klankermayer et al. 2016).

While there have been considerable research efforts to synthesise formaldehyde by the catalytic hydrogenation of CO_2, this is a challenging system and success remains elusive. Research progress to date has been reviewed by Klankermayer et al. (2016). The reaction is strongly endothermic, and it is difficult to avoid further reduction of the very reactive formaldehyde to methanol or methane.

The current state of the art is exemplified by a reaction scheme developed by researchers at RWTH Aachen University, in which CO_2 was hydrogenated in the presence of methanol to produce dimethoxymethane (DMM). The obtained DMM is itself a valuable compound, which can be used in many syntheses as a formaldehyde synthon, but can also be hydrolysed to formaldehyde and methanol (Thenert et al. 2016). The synthesis can be accomplished using either ruthenium or cobalt catalysts with tri-phos ligands in combination with acidic co-catalysts, as shown in Figure 78 below.

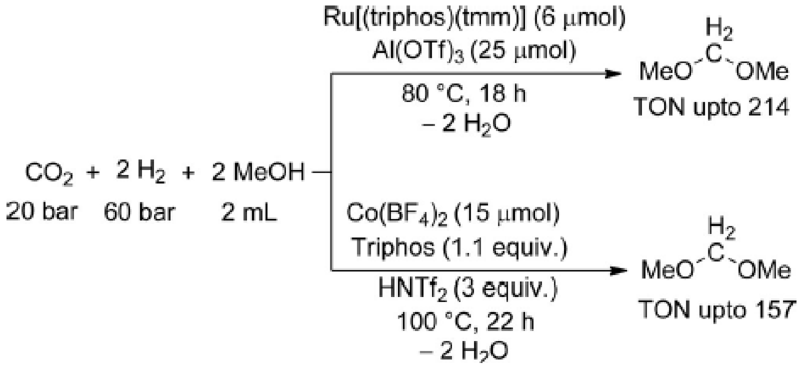

***Figure 78**: Synthesis of DMM from CO_2 using Ru and Co catalytic systems (Dabral & Schaub 2019)*

The presence of the acidic co-catalyst was crucial to allow rapid formation of relatively stable DMM, which prevented further hydrogenation to methanol or methane.

As mentioned, this reaction is strongly endothermic, and additional energy is required for the hydrolysis of DMM to formaldehyde and methanol. It thus has an intrinsically higher energy demand than the current methanol oxidation route, so a competitive process for producing formaldehyde from recycled CO_2 remains a distant prospect (Klankermayer et al. 2016).

8.3.2.1 Victorian Research Context

There is currently no research being done on formaldehyde synthesis in Victoria.

8.3.2.2 ACI Comments

It is certainly possible to produce formaldehyde using CO_2 as a primary product, however the process is complex and expensive. The prospects for economical production of formaldehyde from recycled CO_2 are currently poor, so it is recommended that no local research be undertaken in this area.

8.3.3 Syngas

8.3.3.1 Current Status

Synthesis gas (or syngas), a mixture of CO and H_2, can be produced using CO_2 and methane in a process known as dry reforming, or CO_2 reforming of methane:

$$CO_2 + CH_4 \rightleftharpoons 2CO + 2H_2$$

Syngas is one of the key building blocks of the chemical industry. As shown in Figure 79 below, it can be used to manufacture a diverse range of value-added products.

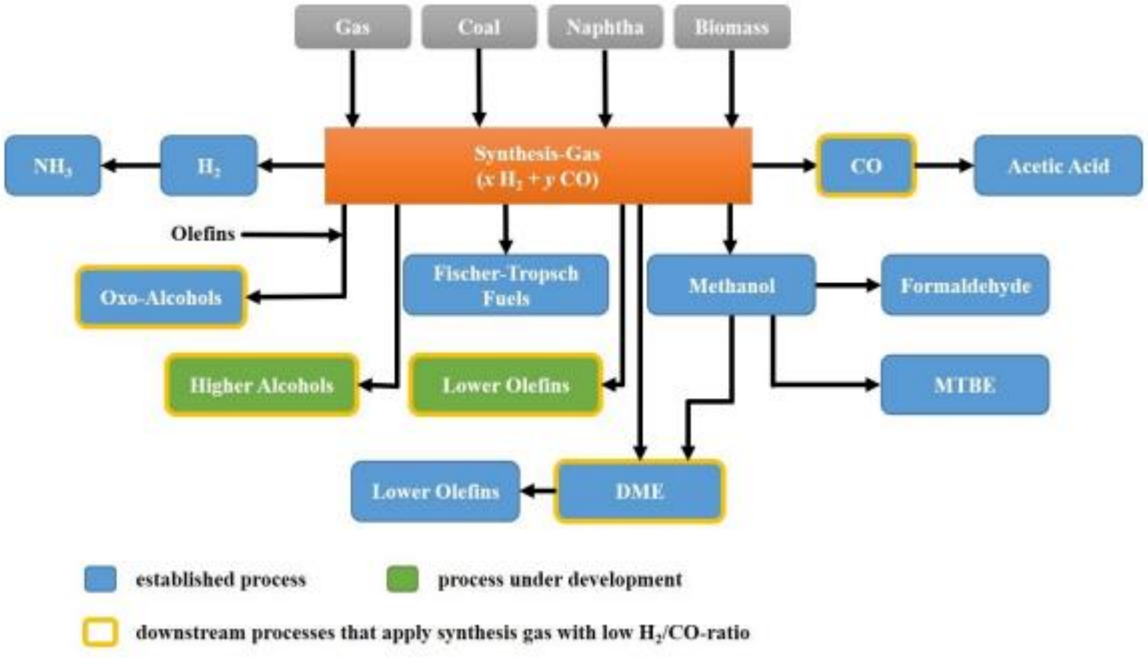

Figure 79: *Downstream processes relying on syngas production (Wittich et al. 2020)*[139]

Syngas is primarily produced through steam reforming of natural gas, also known as steam methane reforming (SMR). Although SMR is a well-established process, it is extremely energy intensive, requiring operating conditions in the region of 1000 ºC and 15-30 atm (Lavoie 2014). It also has the disadvantages that the H_2/CO ratio obtained is very high (>3), excess steam is required, and the catalyst undergoes rapid deactivation due to coke deposition (Mondal 2016).

As indicated in Figure 79, there are some important applications of syngas that require a lower H_2/CO ratio than typically produced through SMR. Dry reforming has a particular advantage in such applications, because it yields syngas with lower H_2/CO ratios, plus it can be employed in water-scarce areas. Research efforts have focussed on the development of catalysts that are resistant to sintering and coke deactivation, and have been reviewed elsewhere (Shah & Gardner 2014).

There are currently two commercial processes involving CO_2 reforming of methane. The SPARG and CALCOR processes (see below) were both developed to prevent coke formation under dry reforming conditions. Unfortunately, these processes are only feasible in certain downstream process scenarios and therefore lack breadth in applicability (Wittich et al. 2020).

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[139] MTBE: 2-Methoxy-2-methylpropane

8.3.3.1.1 SPARG process

In the sulphur-passivated reforming (SPARG) process, natural gas is desulfurised and then mixed with steam to undergo pre-reforming. In the reformer, catalyst is passivated by adding sulphur to the feed to block carbon formation sites (Stal et al. 1992).

8.3.3.1.2 Calcor process

The Calcor process, developed by the German company Caloric, of Munich, is a reforming process combined with CO_2 recovery and CO purification. The raw material, natural or liquid petroleum gas, is mixed with hydrogen, heated prior to catalytic/adsorptive hydration and desulphurisation, then mixed with CO_2. While passing over the catalyst in the reformer tubes, the mixture of CO_2 and feedstock is converted into a synthesis gas comprising CO, H_2, CO_2 and CH_4. Heat for this endothermic reaction is generated by a high-velocity burner firing into the reformer plenum.

After leaving the reformer, the syngas is cooled to ambient temperature prior to undergoing the CO_2 removal and recovery. In this process step, the CO_2 from the reformer flue gas as well as the CO_2 from the syngas are absorbed in packed towers at ambient temperature by a caustic solution (e.g., MEA, MDEA or DGA). In a stripper, the CO_2 is separated from the scrubbing liquid and recycled to the reforming process. The syngas, which now typically consists of 70 % by vol. CO and 30 % by vol. H_2 and still carries traces of CO_2 and CH_4, enters the CO purification step. Further low-temperature purification can yield a CO purity of 99.98 v%, with CH_4 or CO_2 impurities below 1ppm.

In the Calcor Economy version, the CO_2 recovery part is deleted and imported CO_2 is used instead of recovered CO_2. Membranes are used to simultaneously separate H_2 and CO_2 from the CO product, resulting in a simplified design (Teuner et al. 2001).

8.3.3.1.3 Linde process

Most recently, dry reforming of methane has been investigated by the Linde Group at its pilot facility at Pullach, near Munich, shown in Figure 80 below.

***Figure 80:** Linde Group dry reforming pilot plant*[140]

The dry reforming process was developed by Linde in cooperation with its partners BASF and HTE (responsible for catalyst development), Karlsruhe Institute of Technology / KIT (responsible for simulations) and DECHEMA (supplier of materials). The pilot project operated during 2015-17, with financial support from the German Ministry for Economic Affairs and Energy.[141] In 2019, Linde and BASF jointly won the ICIS Innovation Award for Linde's DRYREF™ syngas generation plant utilising BASF's SYNSPIRE™ G1–110 catalyst.[142] Linde is currently seeking an industrial partner to commercialise the DRYREF™ process.

8.3.3.2 Victorian Research Context

CSIRO, in collaboration with RMIT, has developed a novel dry reforming process that can efficiently convert a mixture of CO_2 and CH_4 into syngas at 400-600 ^oC, requiring significantly less energy than the conventional reforming process which requires at least 850 ^oC.

The estimated TRL of the technology is 4. The current internal CSIRO project involves testing of the novel catalyst developed under industrial relevant conditions using the bench scale test rig. Extensive laboratory scale testing of the technology has been carried out in CSIRO up to 100 hours testing. Gas

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[140] http://www.linde.pl/en/news_and_media/press_releases/news_20151015.html

[141] http://www.linde.pl/en/news_and_media/press_releases/news_20151015.html

[142] https://www.icis.com/subscriber/specialpublications/FileAsync?id=W5jYqy5gZvru%252bvykjuekc95XfGdJmC8WAI0alpNPUL9exFcf4OQDUjJ6YuNyAcij

composition with different CH_4:CO_2 ratio and various catalysts have been tested under a broad temperature and gas velocity conditions in a fixed bed reactor.

A provisional patent is being considered. The commercialisation pathway is under consideration which may involve licencing arrangement with catalyst manufacturers, resource producers or operator.

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8.3.3.3 ACI Comments

The techno-economics of the CSIRO-RMIT dry reforming process have yet to be established. While the process is conceptually simple, it is very much dependent on the price of natural gas, which is set by international market forces.

In contrast, production of syngas via gasification of lignite, while requiring temperatures in excess of 1000°C, has the advantage that lignite is an inexpensive raw material that is not subject to market price fluctuations. It is simpler and more cost efficient to capture the resulting CO_2 if the gasification is oxygen-blown and the syngas is converted to hydrogen, rather than combusting the syngas in air. Technical options to make gasification of Victorian lignite with CCS net zero emissions, or even net negative (Kibria et al. 2023a).

Victorian research on lignite gasification laid the groundwork for and supported the successful HESC pilot project. ACI recommends further support for gasification R&D, to better understand the implications of biomass gasification and to create local skills in the emerging hydrogen economy.

8.3.4 Carbon Monoxide

8.3.4.1 Current Status

Carbon monoxide (CO) can be produced from CO_2 by making use of the reverse water-gas shift reaction (RWGS) reaction, in which CO_2 is reacted with hydrogen to produce CO and water:

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

The reaction is endothermic and requires temperatures of above 800 °C to achieve acceptable conversions. Methane is a major product at temperatures of less than 700 °C. Catalyst and process technologies differ substantially from those used in the conventional water-gas shift reaction, as reviewed by Liu et al. (2009).

Carbon monoxide is a higher energy compound and a feedstock for many conventional chemical synthesis processes. As such, RWGS represents an alternative way pathway for valorising waste CO_2 into useful products.

8.3.4.1.1 BASF-Linde-ThyssenKrupp process

In 2013, the German Federal Ministry of Education and Research (BMBF) funded a three year project involving BASF, the Linde Group, ThyssenKrupp and research institutions, to develop a two-stage process for converting CO_2 to CO using RWGS. As shown in Figure 81 below, in the first stage, methane is decomposed at high temperature form hydrogen and granular carbon. In the second stage, hydrogen then reacts with waste industrial CO_2 to produce syngas (CO plus excess H_2) for use as an industrial feedstock (Bode et al. 2014).

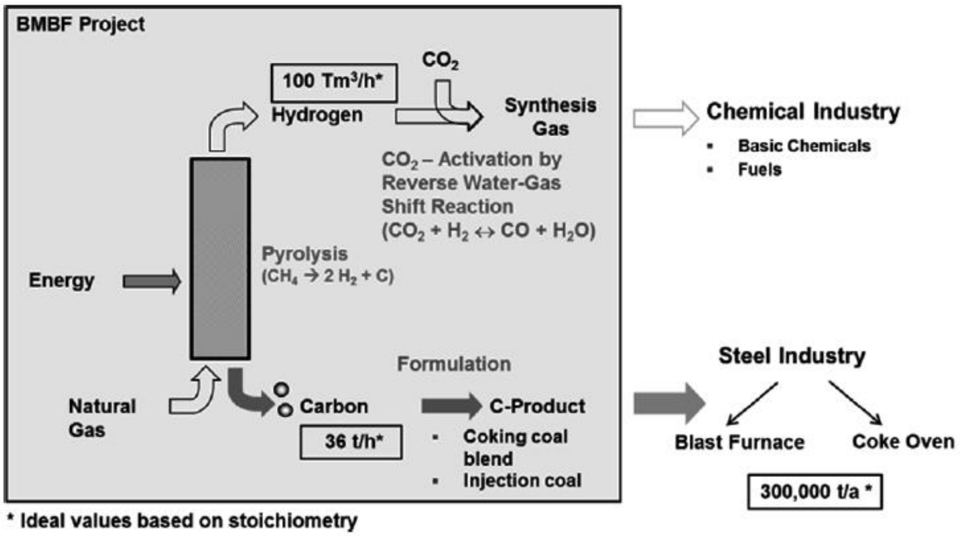

Figure 81: *Methane pyrolysis and conversion of CO_2 by RWGS (Bode et al. 2014)*

In order for the RWGS process to be feasible for adding value to waste CO_2, it is essential that an inexpensive source of CO_2-free hydrogen be used, and that high temperature waste heat be used to drive the reaction. To date, the high cost of hydrogen produced via electrolysis with renewable energy has made this route uncompetitive with state-of-the-art steam methane reforming, which is why such processes have not progressed toward commercial scale (Schwab et al. 2015).

8.3.4.1.2 Topsøe eREACT™ process

To facilitate integration of catalytic reforming with renewable energy, Danish firm Topsøe has developed a catalytic reactor heated by electrical resistance instead of steam (Mortensen et al. 2019), called eREACT™. This reactor can be used for both hydrogen production by RWS and CO production by RWGS.

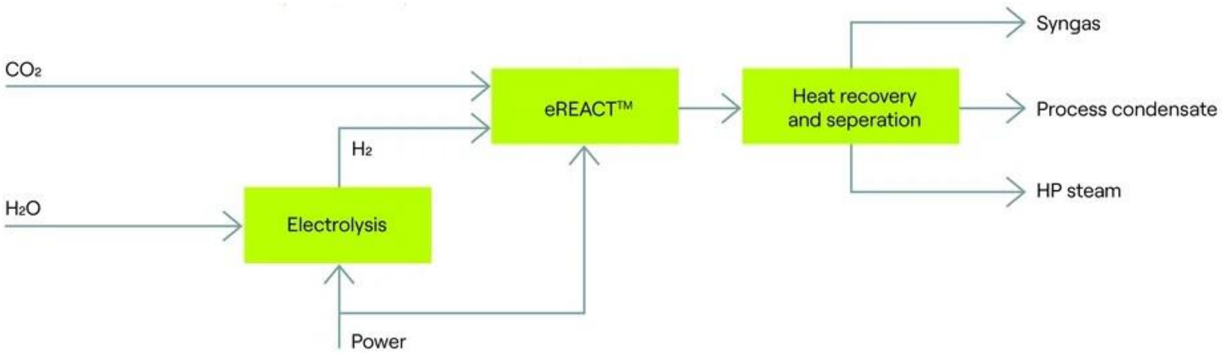

Figure 82: *Production of syngas with renewable energy using Topsøe eREACT™ RWGS system*[143]

The eREACT™ reactor forms part of Topsøe's Green Methanol process, which is currently being commercially implemented in the FlagshipONE project in Northern Sweden (see Section 8.3.5.1.1.2 below).

8.3.4.2 Victorian Research Context

ACI is not aware of any local research on this topic.

8.3.4.3 ACI Comments

Production of carbon monoxide from CO_2 using the RWGS reaction does not make sense when the CO_2 is a by-product of hydrogen synthesis from fossil fuels, as it is simply the process used to generate the hydrogen pushed in reverse. It is only being considered in the context of using renewable energy to produce carbon-based chemicals, but it is energetically expensive. The hydrogen used to split the CO_2 must be very low cost for the downstream products to be cost-competitive, and this is dependent on major improvements in the efficiency of electrolysis.

8.3.5 Methanol

8.3.5.1 Current Status

Methanol, CH_3OH, is a key industrial chemical that is used in thousands of everyday products, including plastics, paints, cosmetics, and fuels. Methanol is also an energy resource used in the marine, automotive, and electricity sectors and an emerging renewable energy resource. As shown in Figure 83 below, the demand for methanol is growing steadily at 3.3% p.a., and is currently 108 Mt/y. Most methanol is produced from natural gas, and current manufacturers have significant capacity to boost output to meet demand, with the total nameplate capacity at 183 Mt/y.[144]

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[143] https://www.topsoe.com/our-resources/knowledge/our-products/equipment/e-react-fuels

[144] https://www.methanol.org/methanol-price-supply-demand

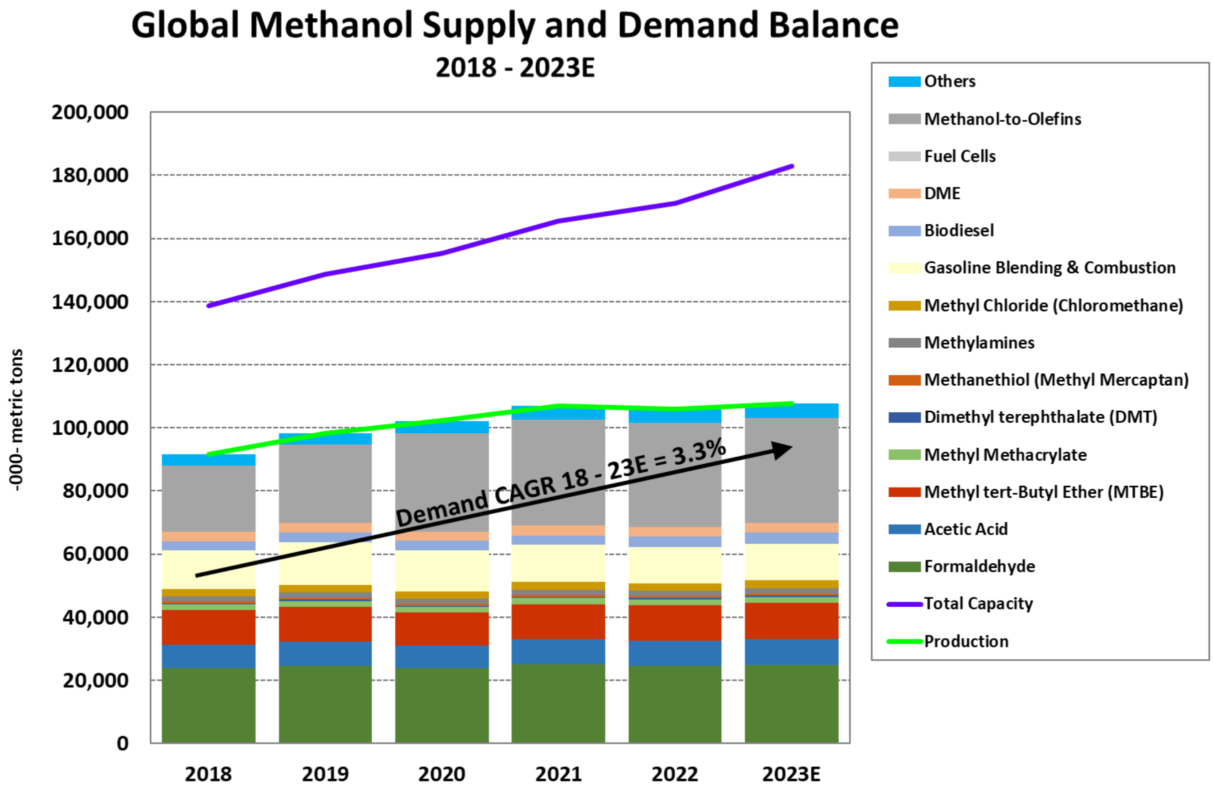

Figure 83: *Historical global methanol supply and demand © Methanol Market Services Asia*

The methanol market is projected to grow from US$30.9 billion in 2023 to US$38.0 billion by 2028.[145] The majority of this growth will be met by increased output from existing natural gas or coal processes. This period will also see substantial growth in capacity of renewable methanol, as both biomethanol (produced from sustainable biomass) and e-methanol (produced from captured CO_2 and hydrogen produced from renewable electricity). With ongoing advancements in technology and increased government support, the capacity of individual renewable plants is expected to rise from 5,000-10,000 t/y to 50,000-250,000 t/y or more over the next five years.[146]

8.3.5.1.1 Hydrogenation of CO

The conventional industrial route for methanol production is by the conversion of synthesis gas (CO + H_2) from fossil feedstocks in the presence of heterogeneous copper-based catalysts (e.g. $Cu/Zn/Al_2O_3$) at elevated pressures (50-100 bar) and temperatures (200-300 ^oC). CO_2 is currently added to adjust the C/H balance of hydrogen-rich synthesis gas mixtures, as it consumes more H_2

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[145] https://www.marketsandmarkets.com/Market-Reports/methanol-market-425.html
[146] https://www.methanol.org/renewable

than CO. It is estimated that about 2 Mt/y of CO_2 is converted into methanol this way (Klankermayer et al. 2016).

8.3.5.1.1.1 CAMERE process

In the late 1990s the Korean Institute of Science and Technology (KIST) developed a process for producing methanol from CO_2 and hydrogen, making use of RWGS to convert CO_2 to CO. This process was known as CAMERE (carbon dioxide hydrogenation to form methanol via a reverse-water-gas-shift reaction). There are two reaction steps involved:

Reverse water-gas shift: $CO_2 + H_2 \rightleftharpoons CO + H_2O$

Methanol synthesis: $CO + 2H_2 \rightleftharpoons CH_3OH$

As shown in Figure 84 below, the CAMERE process involved intermediate H_2O removal to boost the efficiency of the RWGS reaction.

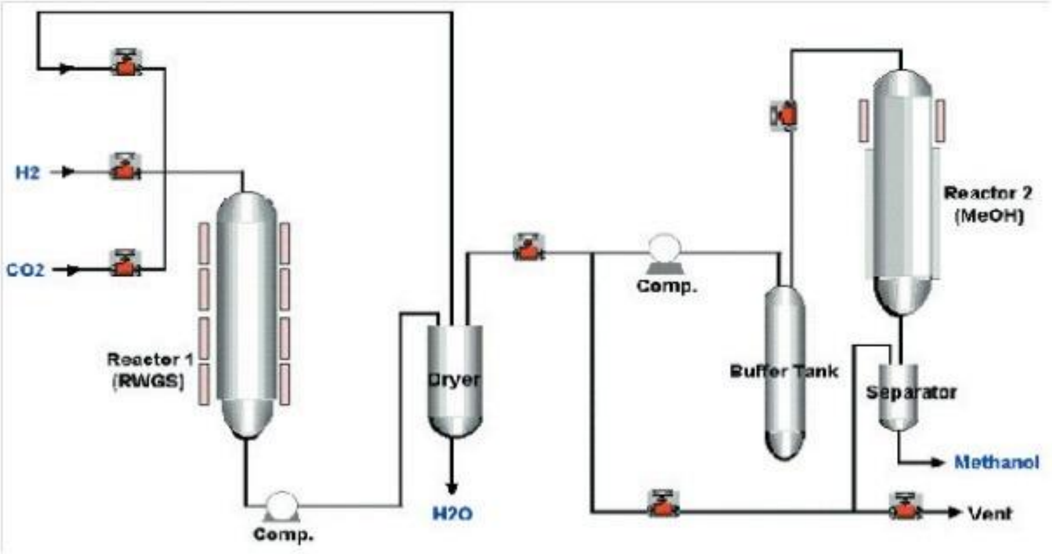

Figure 84: *CAMERE process for methanol synthesis from CO_2 and hydrogen*[147]

The water-gas shift reaction was promoted using a $ZnAl_2O_4$ catalyst (Park et al. 2001), while an active and stable catalyst with the composition of $Cu/ZnO/ZrO_2/Ga_2O_3$ (5:3:1:1) was developed for CO hydrogenation (Joo et al. 1999).

The CAMERE process was demonstrated in a 100 kg/d pilot plant. It was found that the methanol produced was twice as expensive as that produced via the commercial route, so further development was discontinued (Park et al. 2004).

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[147] http://ontobiz.tistory.com/entry/Process-development-for-methanol-Synthesis-from-CO2CAMERE-Process

8.3.5.1.1.2 Topsøe Green Methanol process

Production of synthesis gas (syngas) is an endothermic process, which usually requires energy from combustion of fossil fuels. The Danish catalyst manufacturer, Topsøe A/S, has developed an electrically-powered reverse water-gas shift (RWGS) reactor, called eREACT™, to enable production of syngas from CO_2 and green hydrogen (see Section 8.3.4.1.2 above). This allows Topsøe to produce methanol from CO_2 via conventional hydrogenation of CO, which it promotes as Green Methanol.[148]

Topsøe is an investor and technology partner with the Swedish e-fuels company Liquid Wind, which develops replicable commercial-scale e-methanol production facilities using a standardised and modularised approach.[149] Liquid Wind's first project, FlagshipONE, located in Örnsköldsvik in Northern Sweden, is Europe's largest green e-methanol facility. In December 2022, Danish multinational power company Ørsted acquired FlagshipONE from Liquid Wind to become the sole owner of the project. FlagshipONE is expected to enter into operation in 2025 and will produce around 50,000 tonnes of e-methanol each year.[150] Ørsted is also developing the 300,000 tonne 'Project Star' in the US Gulf Coast area[151] and the 'Green Fuels for Denmark' project in Copenhagen[152], which will both produce significant volumes of e-methanol to enable the decarbonisation of shipping.

In June 2023, Liquid Wind announced that it had signed an agreement with Sundsvall Energi to develop a second 100,000 t facility, FlagshipTWO, which will produce methanol from biogenic CO_2 and green hydrogen.[153] Liquid Wind's third facility FlagshipTHREE is planned to be established in Umeå in connection with the municipal energy company Umeå Energi AB's combined heat and power plant in Dåva, Sweden.[154]

8.3.5.1.2 Hydrogenation of CO_2

Hydrogenation of CO_2 to methanol can be accomplished using well-proven commercial $Cu/Zn/Al_2O_3$ catalysts. However, this reaction requires higher temperatures and pressures than CO hydrogenation, resulting in a higher production cost (Pontzen et al. 2011). This, a priority for research is the development of new catalysts that can operate under milder conditions. Developments in this field have been reviewed by Klankermayer et al. (2018), but are not discussed further here.

8.3.5.1.2.1 Carbon Recycling International process

In Iceland, Carbon Recycling International (CRI) currently operates the George Olah pilot plant for hydrogenation of CO_2 to methanol adjacent to the Svartsengi geothermal power station. CRI was

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[148] https://www.topsoe.com/processes/green-methanol
[149] https://www.liquidwind.se/facilities
[150] https://orsted.com/en/media/newsroom/news/2022/12/20221220609311
[151] https://www.nsenergybusiness.com/news/orsted-maersk-us-power-to-x-facility/
[152] https://orsted.com/en/what-we-do/renewable-energy-solutions/power-to-x/green-fuels-for-denmark#:~:text=The%20Green%20Fuels%20for%20Denmark,first%20ten%20years%20of%20operation.
[153] https://www.liquidwind.se/news/liquidwind-announces-plans-for-flagshiptwo-sundsvall
[154] https://www.liquidwind.se/news/miljotillstandfs3

founded in 2006 and is funded by joint venture partners, which include Methanex, Mitsubishi Hitachi Power Systems, Geely and Zinxin Shanghai Electric. The George Olah pilot plant, shown in Figure 85 below, produces 4,000 t/y methanol, which is exported to the EU market.

Figure 85: *CRI's George Olah methanol pilot plant, Iceland*[155]

The high temperature geothermal steam being tapped at the Svartsengi power station naturally contains a mix of CO_2 and H_2S, which are separated from the steam by pressure swing prior to power generation, with the flue gas being vented. The George Olah methanol plant takes a slipstream of flue gas (90% CO_2, 10% H_2S) and recovers 5500 tCO_2/y food-grade pure CO_2 stream using MDEA solvent capture technology and activated carbon purification. Geothermal electricity is used to power an alkaline, demineralised water electrolysis system to produce hydrogen. The hydrogen and CO_2 are compressed to 80 bar pressure and reacted at 250 ^{o}C over a heterogeneous metal oxide (copper/alumina) catalyst to produce methanol. The reaction is exothermic, so careful temperature control is crucial. The methanol is purified by distillation, and the minor by-products (ethanol, CO, higher hydrocarbons) are disposed along with waste water down a bore hole. Oxygen, a by-product of electrolysis, is vented to atmosphere. The methanol produced is used as a blended component of gasoline and for further conversion to a diesel substitute.

In October 2022 CRI completed commissioning of a new CO_2-to-methanol production facility located adjacent to a coke oven facility in Anyang city, Henan Province, China. The new methanol plant is owned by CRI shareholders Geely Tech., Shuncheng group, Shunju, Shunfeng and MFE Shanghai. The by-product gas from coke manufacture contains CO_2, hydrogen and methane.CRI technology is used to produce 110,000 tons/y methanol from 160,000 tons/y recycled CO_2.[156]

A second CRI plant in China, scheduled to start operation in September 2023, is located at the Shenghong petrochemical complex in Lianyungang, Jiangsu province. The plant can recycle approximately 150,000 t/y of CO_2 and 20,000 t/y of H_2 from onsite processes to produce 100,000 t/y

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[155] www.chemistryworld.com/features/co2-recycling--an-uphill-struggle/3008188.article
[156] https://www.carbonrecycling.is/projects

of methanol. CRI is also is designing a new commercial scale methanol production facility, to be located next to a ferrosilicon plant in Finnfjord, northern Norway. The plant will produce methanol using captured CO_2 from the ferrosilicon plant and hydrogen generated from the electrolysis of water using renewable electricity. [157]

8.3.5.1.2.2 Mitsui Chemicals process

In 2009, the Japanese company Mitsui Chemicals Inc. completed a 100 t/y CO_2-to-methanol pilot plant in Osaka. The process used a proprietary catalyst made from a mixed copper and zinc oxides. The CO_2 was sourced from the exhaust of an adjacent petrochemical factory, while the H_2 was a waste by-product of coke furnaces. In parallel, Mitsui Chemicals was developing photocatalysts for splitting water and solar cell materials for electrolysis on water in order to obtain H_2 from renewable resources (see Figure 86 below). Mitsui Chemicals ranthe plant for 8000 hours to verify the reliability of the catalyst (Quadrelli et al. 2011).

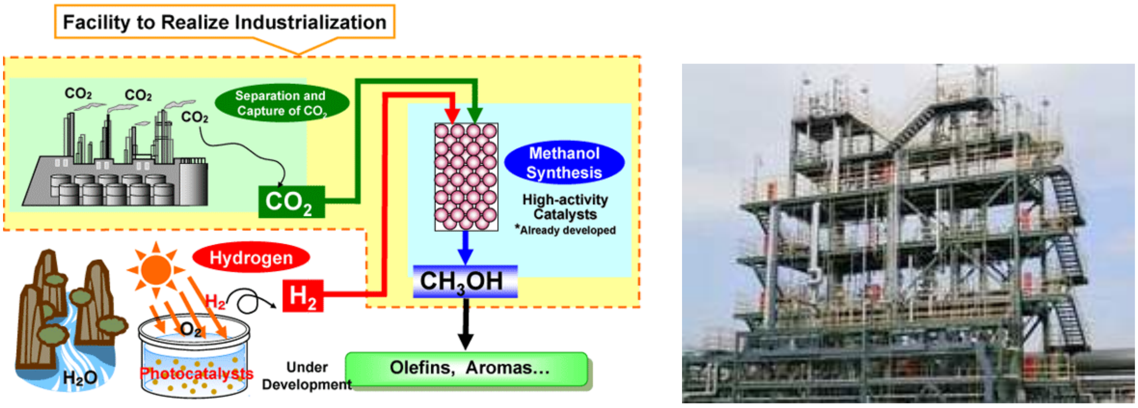

Figure 86: *Mitsui Chemicals CO_2 to methanol pilot plant, Osaka, Japan*[158]

In October 2015, Fairway Methanol LLC, a joint venture between Mitsui and Celanese Corporation, commissioned a 1.3 million t/y methanol plant in Clear Lake, Texas, using natural gas as a feedstock. In April 2021, it was announced that Fairway Methanol would expand capacity to 1.62 million t/y and begin using recycled CO_2 as an alternative feedstock. Approximately 180,000 t/y CO_2 would be sourced from plants at the site owned by Celanese and other companies. Producing methanol using recycled CO_2 was said to be comparable to the normal cost using natural gas.[159]

8.3.5.1.2.3 BSE Engineering process

During 2015-2017, BSE Engineering in Germany developed a process for synthesis of methanol from waste CO_2 and electrolytic hydrogen generated using excess renewable energy. BSE Engineering has developed the concept of small-scale, decentralized production units built near to power plants producing renewable energy for production of hydrogen, as well as large-scale industrial plants producing waste CO_2. The idea is to utilise intermittent renewable energy to produce hydrogen

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[157] https://www.carbonrecycling.is/projects
[158] www.mitsuichem.com/en/release/2008/080825e.htm; www.zeeland.nl/digitaalarchief/zee1001238
[159] https://www.icis.com/explore/resources/news/2021/04/23/10631870/co2-based-methanol-from-us-celanese-jv-resemble-natgas-based-costs/

through discontinuous electrolysis. After this, methanol is produced via the catalytic, exothermic reaction of CO_2 and H_2 using catalysts supplied by BASF.[160]

BSE Engineering created a spin-off company, BSE Methanol in 2019, which signed a FEED contract for the implementation of its first industrial plant in 2021. This plant is expected to commence operation in 2024 with a capacity of 8,000 t/year.[161] To simplify future commercial projects, BSE Methanol offers a skid-mounted, modular installation known as FlexMethanol, which is available in 10 MW and 20 MW configurations.

8.3.5.1.2.4 REintegrate / European Energy process

During the period February 2019 to February 2021, the Danish Energy Technology Development and Demonstration Program (EUDP) funded the Power2Met project. This involved a consortium of industry partners to deliver a power-to-methanol pilot plant for production of methanol from CO_2 and hydrogen. The technology consisted of two main building blocks; a high-pressure HyProvide™ alkaline electrolyser provided by GreenHydrogen and a novel small-scale methanol synthesis plant developed by Aaalborg University, REintegrate and Process Engineering.[162] Aalborg University identified that the CAMERE process (see Section 8.3.5.1.1.1 above) could be made more efficient and can operate under milder conditions by continuous water removal through a combination of membrane reactors and in situ adsorbents within the reactor (Cui & Kær 2019). REintegrate took the lead in demonstrating the process at pilot scale.

Following the successful completion of the Power2Met project, REintegrate was acquired by European Energy, a Danish renewable energy developer. In November 2021, REIntegrate, European Energy and Maersk signed an agreement to supply e-methanol to Maersk's first methanol-powered container ship.[163] Construction of the e-methanol plant began in May 2023 in Kassø, Denmark. The methanol synthesis system will use Clariant´s MegaMax catalyst and have a capacity of 32,000 t/y.[164] Mitsui has acquired a 49% equity interest in the project, and will leverage its expertise in methanol production and sales to enhance the competitiveness of the operation. Production is scheduled to start in 2024.[165]

8.3.5.2 Victorian Research Context

Researchers in Melbourne, at CSIRO and at the University of Melbourne, are investigating strategies to improve the economics of CO_2 hydrogenation to methanol. The approach being developed by CSIRO is to integrate catalytic hydrogenation into the CO_2 capture process, with the aim of eliminating the costs involved in CO_2 recovery, purification and compression. The approach being taken at the

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[160] https://www.greencarcongress.com/2017/08/20170824-basf.html

[161] https://bse-methanol.com/en/unternehmensgeschichte/

[162] https://energiforskning.dk/sites/energiforskning.dk/files/media/document/13.1%20-%20Power2Met_afslutningsrapport_Final.pdf

[163] https://renews.biz/73610/european-energy-acquires-danish-power-to-x-player/

[164] https://www.clariant.com/en/Corporate/News/2023/07/Clariants-MegaMax-catalyst-chosen-by-European-Energy-for-worlds-largest-emethanol-plant

[165] https://www.mitsui.com/jp/en/release/2023/1246818_13943.html

University of Melbourne aims to develop new catalyst and reactor systems to allow the CO_2 hydrogenation reaction to proceed under milder conditions.

8.3.5.2.1 CSIRO – Combined capture and catalytic conversion of CO_2 to methanol

CSIRO is developing a new technology that will allow the separation of CO_2 from waste gas streams (such as those from electricity generation) followed by its *in-situ* catalytic conversion to methanol.

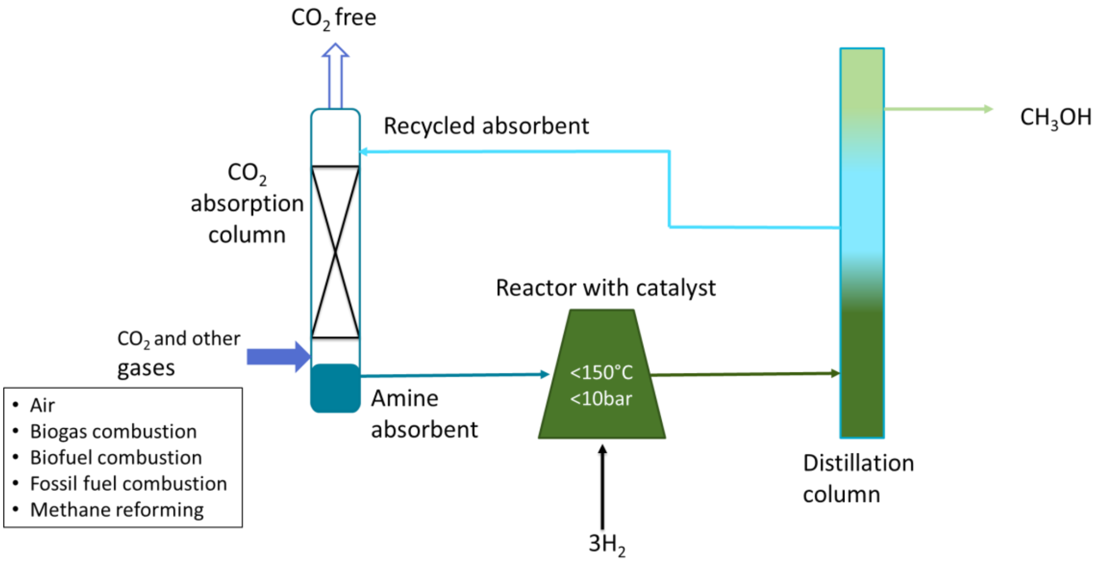

Figure 87: *Process configuration of integrated CO_2 capture and conversion to methanol © CSIRO*

Existing approaches carry out the conversion of CO_2 to methanol via gas phase reactions and heterogeneous catalysis utilising pure CO_2, high temperatures and high pressures. Integration of CO_2 capture and conversion eliminates the CO_2 stripping step that existing approaches require to supply CO_2. It also allows the conversion to proceed in the liquid phase ultimately reducing the temperature and pressure required for the reaction to proceed.

Currently the project is fundamental in nature to understand the chemistry and develop the most efficient and robust combinations of absorbent and catalyst. The project involves collaboration with Professor Liang-Nian He from Nankai University in China. Prof. He is a leader in the activation of CO_2 for conversion to other products (see his recent review on this topic: Song et al. 2023) and is providing advice and guidance to CSIRO researchers.

This research is currently at the fundamental bench scale to develop the necessary catalysts, with a TRL of ~2.

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8.3.5.2.2 University of Melbourne (Webley) – Conversion of CO_2 to methanol and DME

A research team led by Professor Paul Webley at the University of Melbourne is developing catalysts and processes to convert CO_2 and hydrogen to methanol and then on to dimethyl ether (DME). Although the basics of this approach have been well established over many years, the thermodynamics of conventional processes for this reaction leads to low conversions (less than 20 %), pressures of greater than 50 bar, and reasonably high temperatures (> 250 °C). These conditions are chosen to trade off reaction kinetics (improved at higher temperatures) and thermodynamics (improved at lower temperatures and higher pressures). To overcome these limitations, new research is under way in several directions.

a) Developing adsorbent/catalyst hybrid materials which concentrate CO_2 at the catalyst surface to increase the local partial pressure of CO_2 even at low bulk gas conditions. To do this, hydrotalcite supports for Cu/ZnO catalysts have been developed and synthesis conditions have been optimised to provide high methanol selectivity (Fang et al. 2019).

b) Developing a liquid phase reaction approach which dramatically lowers the temperature and pressure conditions needed. This approach proceeds through a formate chemistry mechanism and allows the reaction to proceed at significantly lower temperatures and pressures. The chemistry of this process is being studied to understand its scale-up potential and economics (Ye et al. 2023).

c) Developing Nickel-Gallium supported catalysts for methanol synthesis from CO_2 and H_2. Recent published literature has suggested that Nickel-Gallium systems can potentially provide much higher conversions at lower temperatures than conventional Cu/ZnO systems. These systems are being explored using a variety of synthesis methods and catalyst supports to understand how the catalyst behaves and how the reaction kinetics may be improved through synthesis methods (Men et al. 2020).

d) Hybrid adsorbent-catalyst systems for methanol to DME conversion. Conversion of methanol (which is not a useful fuel) to DME (which is a replacement fuel for LPG or even diesel) is equilibrium limited. Removing water as the methanol is dehydrated may "push" the equilibrium to the right to dramatically increase conversion. A research program is under way, utilising University of Melbourne skills in catalysis and adsorption, to develop hybrid TSA/reactor and PSA/reactor schemes using admixtures of catalysts and adsorbents (Redondo et al. 2019; Mazur et al. 2019; Hastadi et al. 2022).

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8.3.5.3 ACI Comments

Methanol is such an important industrial chemical that it is not surprising that its production from recycled CO_2 *has advanced quickly to pilot scale. However, these advances are based on the use of well-proven commercial* $Cu/Zn/Al_2O_3$ *catalysts, which require elevated temperatures and pressures for efficient operation. These catalysts are the same as those used in the current industrial process for conversion of synthesis gas to methanol, hence the hydrogenation of* CO_2 *to methanol is a relatively mature technology, with a TRL of 7 – 8.*

However, in most instances this process will not be cost-competitive with existing fossil-derived methanol. The exception to this is CRI in Iceland, which uses cheap geothermal electricity to produce hydrogen by electrolysis.

Hence, there is great research interest in developing improved systems that will enable the hydrogenation of CO_2 *to methanol under milder operating conditions. For example, C4X has developed an alternative, lower-energy route, with the synthesis of methanol via ethylene carbonate as an intermediate.*

Techno-economic studies of methanol synthesis have suggested that an inexpensive source of CO_2*-free hydrogen is essential, and the poor process economics could be improved by upgrading methanol to higher-value derivatives such as dimethyl carbonate (DMC – see Section 8.1.2.1.2 above) and dimethyl ether (DME).*

The value of methanol as a key product and intermediary is such that research on more cost-effective synthesis routes is almost obligatory. The research currently being led by Professor Webley at the University of Melbourne should be supported and expanded.

8.3.6 Ethanol

8.3.6.1 Current Status

Ethanol (CH_3CH_2OH) is a clear, colorless renewable fuel made by yeast fermentation of plant-derived sugars. The largest single use of ethanol is as an engine fuel and fuel additive, due to it having a higher octane number than gasoline. In 2022, global production of fuel ethanol amounted to 28,160 million gallons (106.6 billion litres), with the United States and Brazil the largest producers (Figure 88).

Despite ethanol being a renewable fuel, it has the major disadvantage of competing with food supply for arable land.

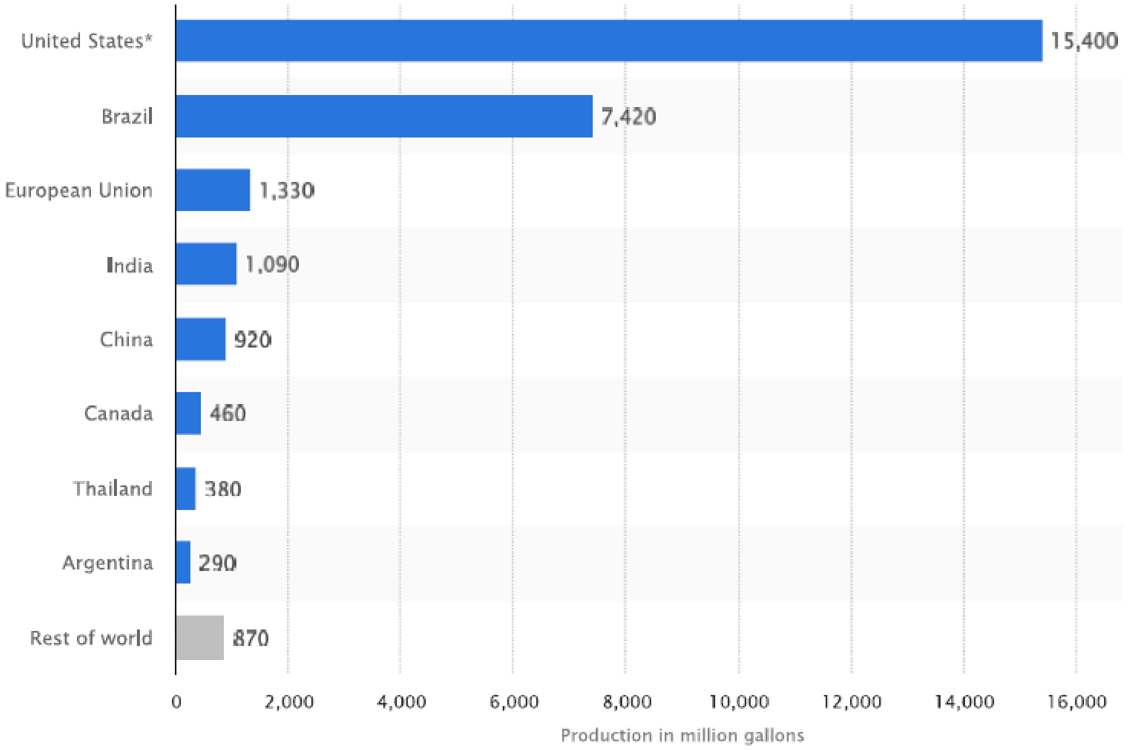

Figure 88: *Global production of fuel ethanol in 2022 (Statista 2023)*

Apart from its use as a fuel, ethanol is also a promising hydrogen carrier and a versatile building-block for chemicals, fuels and polymers. One of the most prospective uses for renewable ethanol is for conversion to ethylene. At present, about 75% of petrochemical products are produced from ethylene, including acetaldehyde, acetic acid, ethylene oxide, ethylene glycol, ethylbenzene, chloroethanol, vinyl chloride, styrene, ethylene dichloride, and vinyl acetate, etc. It is also used in the manufacture of widely-used polymers, such as polyethylene, polyvinyl chloride, polystyrene, etc. (Zhang & Yu 2013).

Dehydration of ethanol to ethylene is a well-established technology that is commercially available, e.g., Scientific Design Company (Little Ferry, N.J.), Lummus Technology (Houston, TX) and Braskem (Brazil). For example, Braskem is operating a bio-based ethylene plant, located in the Petrochemical Complex of Triunfo, Rio Grande do Sul, Brazil, with a capacity of 260,000 t/y. Braskem also produces bio-based polyethylene at this facility, and has manufactured more than 1.2 million tonnes since 2010. Braskem claims that each tonne of plastic resin made from renewable feedstock represents the removal of 3 tonnes of CO_2 from the atmosphere.[166]

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[166] https://www.braskem.com.br/europe/news-detail/braskem-expands-its-biopolymer-production-by-30-following-an-investment-of-us-87-million

The combination of large market potential for ethylene and limited land area available for production of bio-ethanol has stimulate intense interest in alternative routes for ethanol synthesis. In the context of this report, two potential routes should be mentioned: conversion of syngas to ethanol and hydrogenation of CO_2 to ethanol.

The biological conversion of syngas to ethanol has been developed as a commercial process by LanzaTech (described in Section 6.3.2.1.1 above). LanzaTech has established four commercial installations in China and one in Belgium, with another in India under construction, with production capacities of between 46,000 and 64,000 t/y ethanol.

A variety of catalytic routes for conversion of syngas to ethanol have also been investigated, either directly or indirectly via methanol or dimethyl ether (DME), as summarised in Figure 89 below. To date, the catalysts used in these reactions have suffered from low selectivity, which reduces the efficiency of ethanol production (Haro et al. 2013).

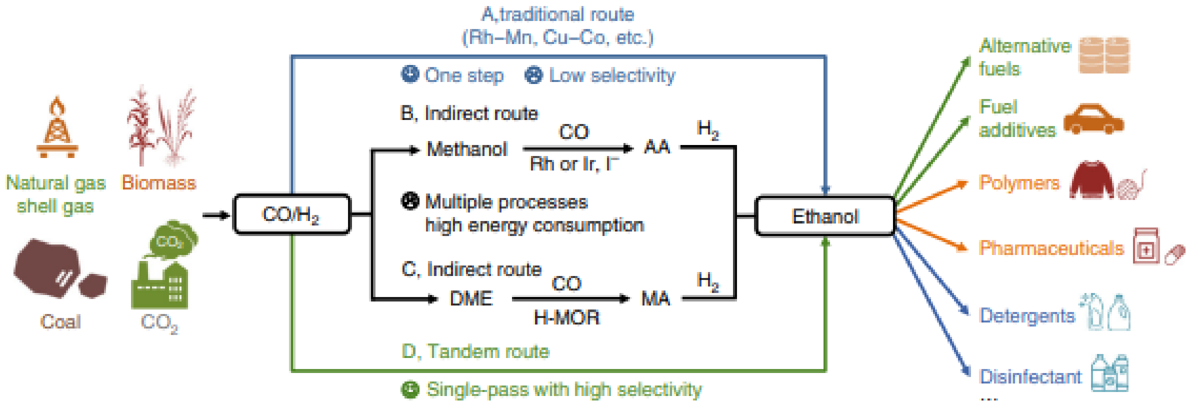

Figure 89: *Routes for conversion of syngas to ethanol (Kang et al. 2020)*

A promising new development in this field was reported by Kang and co-workers at Xiamen University, China, who developed a trifunctional tandem catalyst system composed of potassium-modified $ZnO–ZrO_2$, modified zeolite mordenite, and Pt–Sn/SiC. This combination was found to work synergistically in a single reactor to convert syngas to ethanol with a selectivity of 90% (Kang et al. (2020).

The second route of interest, hydrogenation of CO_2 to ethanol, is economically attractive but is scientifically challenging because of the requirement of forming C–C bonds while retaining some of the C–O bonds (An et al. 2019). At the present time, it is a great challenge to obtain high selectivity to ethanol and high CO_2 conversion using traditional heterogeneous catalysts. The traditional candidate catalysts tend to produce CH_4 or CO as co-products, so great efforts have been expended to identify new catalyst compositions and configurations – reviewed in Ali et al. (2022).

In a promising new development, Ding and co-workers at Nanjing University, China, reported a new catalyst system comprising Cu nanoparticles embedded in crystalline particles of Na-Beta zeolite. This catalyst achieved 100% specificity of ethanol from CO_2, and a yield of ~14% in a single pass at

300 °C, 2.1 MPa. The three-dimensional arrangement of the irregular Cu nanoparticles within the zeolitic framework was thought to strongly constrain the CO_2 reactions and block by-product formation (Ding et al. 2020).

8.3.6.2 Victorian Research Context

ACI is not aware of any relevant research on this topic being undertaken in Victoria.

8.3.6.3 ACI Comments

Alternative routes for production of ethanol, as a fuel and feedstock for chemical conversion, are of immense commercial significance. Efficient synthesis of ethanol from renewable biomass or from captured CO_2 *is essential for building a low-emission chemicals industry without further encroaching on valuable agricultural land.*

LanzaTech's gas fermentation process for converting syngas to ethanol has a TRL of 9, and commercially operating at scales up to 64,000 t/y. Gasification of biomass with CCS would provide a bio-syngas with a low carbon footprint.

While the catalysts required for hydrogenation of CO_2 *to ethanol are currently at TRL 2-3, they have the potential to be scaled up and commercialised very quickly once an optimal formulation has been identified.*

This is a topic of direct significance for manufacturing in Victoria. Qenos in Altona is the largest producer of petrochemicals and plastics in Australia today. Qenos processes ethane feedstock sourced from Bass Strait into ethylene for its downstream polyethylene plant, which produces around 105 kt/y of high density polyethylene.[167] *In 2021, the Altona Refinery was closed, reducing the availability of feedstock to the Qenos plant. Consequently, Qenos mothballed one of its two ethylene plants and one of its two polyethylene plants, resulting in a 15% reduction in total Australian polyethylene production.*[168]

The future of polyethylene production at the Qenos Altona plant is further jeopardised by the declining output from the Bass Strait gas fields. The number of producing wells is in steady decline, falling from 122 in 2010 to 68 today. In March 2023, the gas industry announced that the number of operational wells in the Bass Strait is expected to almost halve by winter 2024.[169]

As an alternative to opening up new gas fields in Victoria, it is important to investigate alternative sources of ethylene for manufacture of polyethylene. As such, ***local R&D on production of industrial ethanol via syngas conversion or hydrogenation of*** CO_2 ***is of vital strategic importance to the manufacturing industry in Victoria and Australia. ACI recommends support***

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[167] https://www.qenos.com/internet/home.nsf/web/OurPlants

[168] http://quenos.com/internet/home.nsf/0/6C29EE4529E9F9BBCA2586DA0005EF13/$file/Qenos%20Media%20Release_Qenos%20Reconfigures%20Altona%20Manufacturing%20Facilities.pdf

[169] https://www.afr.com/companies/energy/exxon-warns-of-dwindling-bass-strait-gas-20230322-p5cuce

for research in Victoria on efficient catalysts for conversion of CO_2 to ethanol, so as to be well positioned to capitalise on any breakthroughs, either locally or internationally.

8.3.7 Hydrocarbons

8.3.7.1 Current Status

There is a great deal of interest in converting recycled CO_2 into value-added hydrocarbons, such as liquefied petroleum gas (LPG), lower olefins (ethylene, propylene and butylene), gasoline, aromatics, etc. Given the important role played by such hydrocarbons in the modern economy, it is no surprise that a range of different technologies are available.

In general, there are two main routes that could be adopted for synthesis of hydrocarbons from recycled CO_2. The first is based on the conversion of syngas to hydrocarbons using the well-established Fischer-Tropsch synthesis route, while the second is based on the conversion of methanol to hydrocarbons. Each of these is discussed below.

8.3.7.1.1 Fischer-Tropsch synthesis

Fischer-Tropsch synthesis (FTS) provides a way to produce liquid fuels and chemicals from coal, natural gas and biomass. The FTS process converts syngas ($CO + H_2$) in the presence of a catalyst (Fe or Co) into a mixture of predominantly linear alkanes and alkenes (Yang et al. 2017).

$$\text{Alkanes (parrafins):} \qquad nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$$

$$\text{Alkenes (olefins):} \qquad nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O$$

The FTS reaction is strongly exothermic and the product distribution is sensitive to temperature and pressure. In order to maximise the desired products and maintain catalyst stability, heat exchange and temperature must be precisely controlled (Venvik & Yang 2017).

As a general process technology, FTS is fully commercialised and implemented on a global scale to produce a variety of hydrocarbon products. Sasol in South Africa utilises gasification and FTS processes to produce diesel fuel from coal. Shell’s Pearl GTL (gas-to-liquid) facility at Ras Laffan in Qatar produces up to 140,000 barrels of liquid fuels per day (Jarvis & Samatli 2018).

Recycled CO_2 can be converted to value-added hydrocarbon products using FTS by first converting it to syngas, via dry reforming of methane or the reverse water-gas shift (RWGS) reaction (as described above), followed by FTS.

8.3.7.1.1.1 Solarbelt FairFuel gGmbH

The world's first plant for the production of CO_2-neutral e-kerosene, in the north-German town of Werlte, was opened in October 2021. Owned and operated by Solarbelt FairFuel gGmbH, a sister company of atmosfair, a German non-profit organisation. The plant produces synthetic crude oil by means of RWGS and FTS using CO_2 from biogas or DAC. Electrical energy is supplied by wind energy plants in the surrounding area, and green hydrogen is produced using a Siemens Silyzer 200

PEM electrolyser.[170] The plant is designed to produce approx. 350 tons/y of synthetic crude, which will be transported to the Heide refinery near Hamburg for conversion into eight barrels/d of e-kerosene (Jet A1). Although the cost of the e-kerosene is very high, at over €5/litre, the Lufthansa Group has committed to an annual minimum purchase of 25,000 litres for at least five years.[171]

8.3.7.1.1.2 Carbon Engineering

A similar approach is being pursued by the Canadian company Carbon Engineering, which is developing a process called AIR TO FUELS™. This combines Direct Air Capture, green hydrogen production, and FTS to produce drop-in compatible gasoline, diesel and aviation fuel. Instead of using conventional FTS catalyst, which creates a wax by-product that requires additional processing, Carbon Engineering uses a proprietary system developed by Greyrock (California, USA) which does not produce wax (Zhu 2018).

In August 2023, US oil giant Occidental Petroleum Corp. announced that a wholly owned subsidiary has agreed to acquire all the outstanding equity of Carbon Engineering Ltd. for approximately US$1.1 billion. Upon closing, Carbon Engineering will become a wholly owned subsidiary of Oxy Low Carbon Ventures. Carbon Engineering and Occidental have been working together to build Stratos, the world's largest DAC plant, which is expected to be commercially operational in mid-2025, in Ector County, Texas. Occidental and Carbon Engineering are also adapting Stratos' front-end engineering and design study for a DAC plant to be built at King Ranch in Kleberg County, which is part of the South Texas DAC Hub.[172]

8.3.7.1.1.3 Velocys

Another approach to implementing FTS for smaller-scale recycled CO_2 sources, such as small gas and biomass resources, is the development of compact microchannel reactor systems. The main exponent of this approach is Velocys, from Plain City, Ohio, which has developed a microchannel FTS reactor. This involves thousands of process channels with dimensions in the millimetre range, which are filled with catalyst, and constructed immediately adjacent to water-filled coolant channels. *In situ* regeneration of highly active cobalt-based catalysts was shown to be effective after 650 days on stream in a laboratory microchannel unit (LeViness et al. 2014).

In December 2022, Velocys was awarded a grant of £2.5 million from the UK Department for Transport's Advanced Fuels Fund to contribute its technology to an e-fuels project in the UK. The funding will be used in conjunction with the e-fuels project's partners (Clariant Catalysts, Technip Energies and British Airways) to conduct feasibility, technical validation, site selection and pre-FEED engineering for such a project, to make sustainable aviation fuel from carbon dioxide and hydrogen.[173]

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[170] https://www.hydrocarbonprocessing.com/news/2021/10/siemens-power-to-kerosene-project-begins-operations
[171] https://www.greenairnews.com/?p=1803
[172] https://www.oxy.com/news/news-releases/occidental-enters-into-agreement-to-acquire-direct-air-capture-technology-innovator-carbon-engineering/
[173] https://velocys.com/projects/e-fuels-2/

Velocys has built a 4,830 m^2 reactor core assembly facility in Columbus, Ohio with sufficient production capacity to meet projected orders until 2028. The new site will be able to produce approximately 12 reactors a year and will house all of Velocys' reactor core assembly and catalysis operations.[174]

8.3.7.1.1.4 Nordic Electrofuel

Nordic Electrofuel, based in Baerum, Norway, has developed a novel fuel generation system that combines partial oxidation and RWGS (POX-rWGS) reactor design for producing e-fuel from CO_2 and hydrogen (Løvstad et al. 2023). In July 2023, Nordic Electrofuel was awarded a €40 million grant to construct a demonstration plant in Porsgrunn, Norway for production of Sustainable Aviation Fuel (SAF).[175] The process will use the POX-rWGS-reactor to convert CO_2 to syngas, then FTS will be employed to produce synthetic crude. The plant is named E-fuel1 and is designed for a yearly production capacity of 10 million litres of synthetic fuels, starting from 2025.[176]

The synthetic crude produced by Nordic Electrofuel will be upgraded by P2X-Europe GmbH (Hamburg, Germany) to e-SAF.[177]

8.3.7.1.2 Methanol-to-hydrocarbon synthesis

A relatively recent approach is the synthesis of hydrocarbons from methanol, using the methanol-to-olefin, methanol-to-propene and methanol-to-gasoline processes. Many institutions and companies have put great effort to the research of methanol-to-hydrocarbons reaction since it was first proposed by Mobil Corporation in 1977, and significant progress has been achieved with respect to the reaction principle, catalyst synthesis, and process research and development (R&D). These developments have been reviewed elsewhere (Stöcker 2010) and so the details involved not be discussed further here.

8.3.7.1.2.1 Haru Oni e-gasoline demonstration plant

A consortium comprising HIF Global, Porsche, Enel, ENAP, Siemens Energy, ExxonMobil and Empresas GASCO has built Haru Oni, the first commercial-scale renewable methanol-to-gasoline plant, located in Punta Arenas, Chile. The process uses wind energy and electrolysis to produce green hydrogen, and captures CO_2 from a biogenic source and/or DAC. Technology for methanol production is supplied by Johnson Matthey[178], and carbon neutral gasoline (e-gasoline) and carbon neutral liquefied gas (e-LG) are produced using ExxonMobil methanol-to-gasoline technology.[179]

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[174] https://velocys.com/technology/

[175] https://nordicelectrofuel.no/wp-content/uploads/2023/07/Press-release-Nordic-Electrofuel-getting-EU-Innovation-fund-grant-40M-Euro.pdf

[176] https://nordicelectrofuel.no/what-we-do/

[177] https://nordicelectrofuel.no/wp-content/uploads/2023/06/Press-Release-P2X-Europe-Nordicelctrofuel_23.06.2023.pdf

[178] https://matthey.com/news/2021/jm-technology-selected-for-worlds-first-climate-neutral-methanol-plant

[179] https://hifglobal.com/location/haru-oni/

Figure 90: *Haru Oni eFuels demonstration plant*[180]

Johnson Matthey is a leading supplier of methanol catalysts and process technology, and has been commercialising its CO_2-to-methanol technology since 2011. Johnson Mattey licensed its patented methanol technology (Early 2019; Early & Turnbull 2023 – see Figure 91) and its newest catalyst, KATALCO 51-102, for the Haru Oni project. [181]

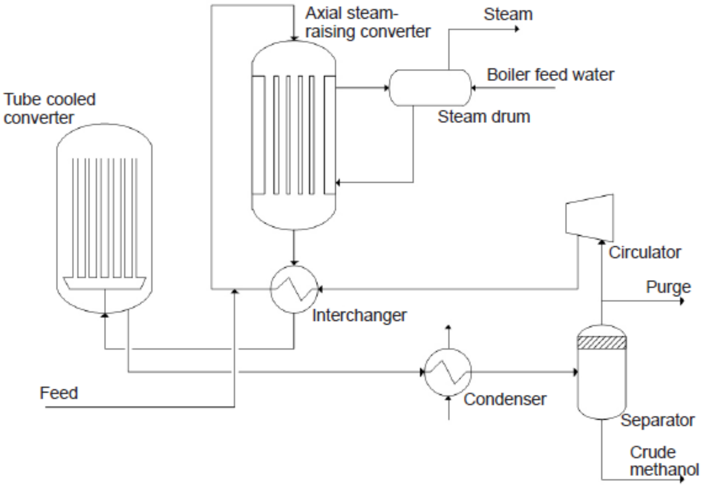

Figure 91: *Johnson Matthey Combi Loop methanol synthesis (Sheldon 2017)*

The methanol is converted to eFuel using the ExxonMobil methanol-to-gasoline process (shown in Figure 92 below). Methanol is first dehydrated to dimethylether (DME); an equilibrium mixture of methanol, DME and water is then converted to light olefins (C_2-C_4). A final step synthesizes higher olefins, n/iso-paraffins, aromatics and naphthenes. A shape-selective catalyst limits the synthesis

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[180] https://www.hydrogeninsight.com/transport/first-batch-of-e-fuel-made-from-green-hydrogen-and-captured-co2-heading-from-chile-to-uk-for-porsche-testing/2-1-1425160

[181] https://matthey.com/news/2021/jm-technology-selected-for-worlds-first-climate-neutral-methanol-plant

reactions to 10 carbons. The reaction product is separated into gas, raw gasoline and water. Raw gasoline is separated into liquefied gas (LG), light gasoline and heavy gasoline; heavy gasoline is hydro-treated to reduce durene content, then heavy and light gasoline are re-combined into finished gasoline.[182]

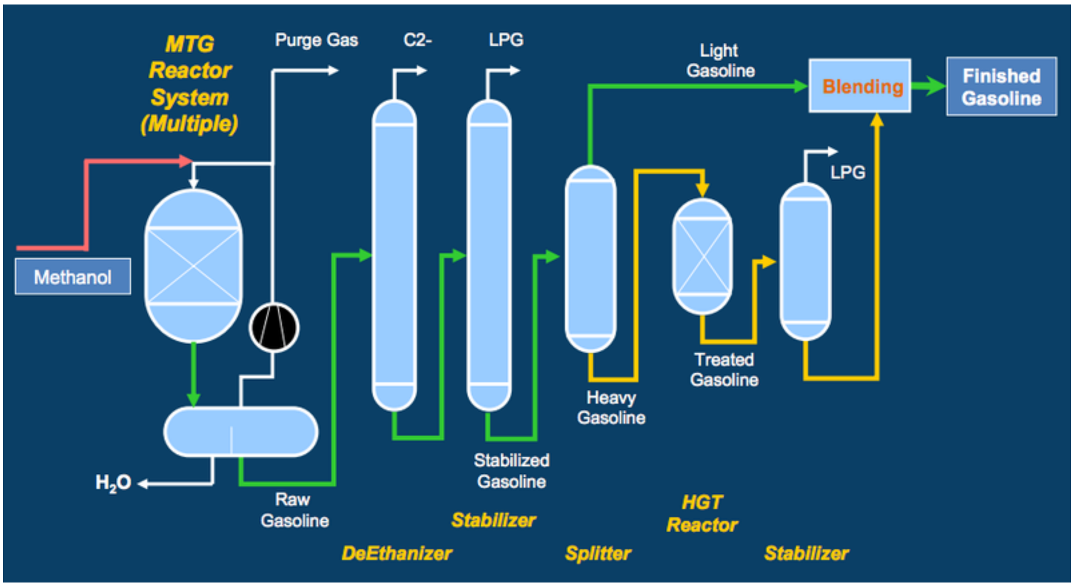

Figure 92: *ExxonMobil methanol-to-gasoline process*[183]

Haru Oni will initially produce 350 tons per year of e-methanol and 130,000 liters per year of e-gasoline. In March 2023, the first batch of 2,600 litres was shipped to the Haltermann Carless refinery in Harwich, eastern England, for testing to ensure it can be used in unmodified engines. It is expected that plant capacity will be increased in two phases, to about 55 million litres of e-fuels a year by 2025 and more than 550 million litres by 2027.[184]

8.3.7.1.2.2 Metafuels "aerobrew" process

A new strategy for producing fuels from e-methanol was recently announced by the Swiss cleantech firm Metafuels AG. Working with the Paul Scherrer Institute in Switzerland, Metafuels has developed a copper-based metal organic framework (MOF) catalyst for converting methanol to aviation fuel (Peoxoto Esteves et al. 2023). The MOF affords high selectivity and yield, in a process that Metafuels dubs "aerobrew".[185] In June 2023, Metafuels and European Energy (see Section 8.3.5.1.2.4) announced a collaboration in which European Agency will provide e-methanol as a source of renewable aviation fuel using the aerobrew process.[186]

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[182] https://www.greencarcongress.com/2012/06/sundrop-20120628.html
[183] https://www.greencarcongress.com/2012/06/sundrop-20120628.html
[184] https://www.hydrogeninsight.com/transport/first-batch-of-e-fuel-made-from-green-hydrogen-and-captured-co2-heading-from-chile-to-uk-for-porsche-testing/2-1-1425160
[185] https://metafuels.ch/
[186] https://bioenergyinternational.com/european-energy-and-metafuels-eye-danish-methanol-to-jet-project/

8.3.7.2 Victorian Research Context

Professor Alan Chaffee at Monash University, School of Chemistry, has identified novel metal organic framework (MOF)-derived catalyst designs for the targeted synthesis of methane or hydrocarbon liquids (Alqarni et al. 2021; Alqarni et al. 2022). These catalysts have been demonstrated to provide order of magnitude superior performance relative to benchmark (commercial) Fischer-Tropsch catalysts. Factors which contribute to their exceptional activity are the nanoparticulate size of the active metal species, together with their exceptionally well dispersed arrangement on the residual carbon, which acts as a support material.

These researchers are collaborating with VTT Technical Research Centre of Finland to develop improve adsorbents for CO_2 capture from air (and thus improve the energy efficiency of this overall approach). Note that VTT is a collaborator with the Finnish company Soletair, which has already demonstrated the concept of CO_2 capture from air, coupled with H_2 from solar-based electrolysis of water, followed by Fisher Trospch-like synthesis to generate liquid fuels. Soletair used existing materials (adsorbents and catalysts) for its demonstration (Vázquez et al. 2018).

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8.3.7.3 ACI Comments

The development of compact microchannel reactor systems, as is being done by Velocys and others, is based on the premise that the required hydrogen will be produced from excess renewable energy on an intermittent basis. This concept was developed before the advent of economical battery systems, which should eventually do away with the notion of 'excess renewable energy'. It is not recommended that this line of research be pursued in Victoria.

As discussed in Section 8.3.5 above, methanol is a key chemical target for CO_2 recycling, but should be further upgraded to improve the process economics.

The current project at Monash University, with links to the Finnish company Soletair, is in a position to develop novel intellectual property in catalysts for hydrocarbon synthesis. This R&D initiative is a good first step toward methanol-to-olefins. ***ACI recommends that this be viewed from the strategic perspective of an R&D pipeline of CO_2 to methanol to value-added products, with support provided on a portfolio basis.***

8.3.8 Methane

8.3.8.1 Current Status

Methane, the main component of natural gas, can be produced by the exothermic hydrogenation of CO_2 in a process called CO_2 methanation, or Sabatier synthesis:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

The reaction is carried out at temperatures of around 250-550 °C over a Ni, Rh or Ru based catalyst (reviewed in Roy et al. 2018). Synthetic natural gas (SNG), which is predominantly methane, can be produced following CO_2 methanation by removal of water and residual CO_2. SNG is highly flexible in application and can be utilised for heating, transportation, electricity generation or as a feedstock for the chemical industry. The SNG can be stored and distributed in established natural gas pipework systems, making SNG an effective way to recycle CO_2 and store excess renewable energy.

Production of SNG from coal and biomass is a well-established technology, with a variety of commercial processes in operation since the 1950s (Kopyscinski et al. 2010). The Great Plains Synfuels Plant in Beulah, North Dakota, which has been operational since 1984, is the only commercial plant in the United States producing SNG from coal, specifically, lignite. The plant produces more than 54 billion standard cubic feet of natural gas annually and sends as much as 95 million standard cubic feet per day of CO_2 via a 205-mile pipeline to the Weyburn Oil Field in southwestern Saskatchewan, Canada, for enhanced oil recovery (EOR) (Chandel et al. 2009).

The Great Plains Synfuel Plant produces SNG using the steam-oxygen process, in which the lignite is gasified with steam and oxygen. The essential components of the process, shown in Figure 93 below, are the air separation unit, the gasifier, the water-gas shift reactor, syngas cleanup, and the methanation reactor.

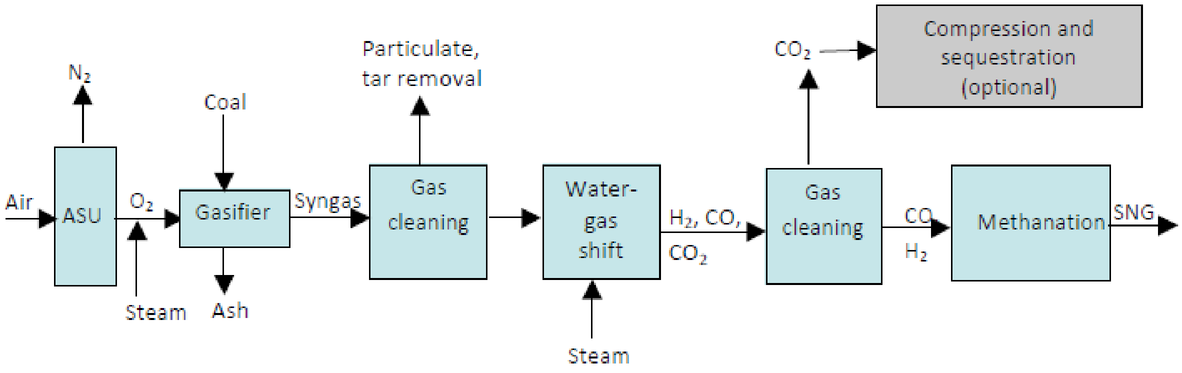

Figure 93: *Block diagram of the steam-oxygen gasification process (Chandel et al. 2009)*

The steam-oxygen gasification process produces carbon monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2), methane (CH_4), and higher hydrocarbons such as ethane and propane. At higher temperatures and pressures, the major products are CO and H_2 (i.e., syngas). Three moles of H_2 are required to react with each mole of CO to produce one mole of CH_4. The concentration of H_2 in syngas is increased by a step called the water-gas shift reaction, which is followed by gas cleaning. The cleaned gas reacts in the methanation reactor in the presence of a catalyst to produce CH_4 and H_2O. Removal of water by condensation and polishing, if required, results in SNG.

Production of SNG using recycled CO_2 and hydrogen from low-emission sources is mainly accomplished using nickel catalysts (Younas et al. 2016). A wide variety of experimental systems have been investigated internationally, as reviewed by Gahleitner (2013).

8.3.8.1.1 ETOGAS process

Currently, the state-of-the-art process is that of ETOGAS, based on a proprietary catalytic reactor technology. The basic concept of the ETOGAS process is shown in Figure 94 below.

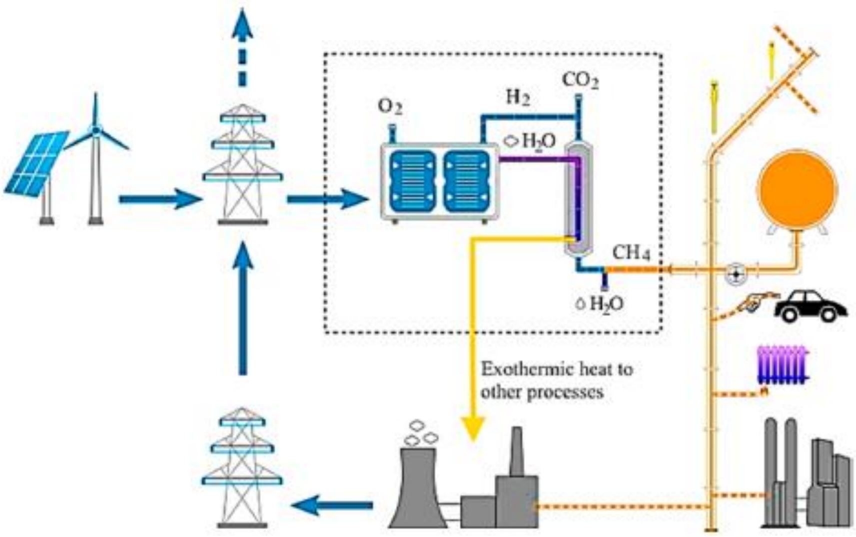

Figure 94: *ETOGAS Power-to-Gas process concept (Younas et al. 2016)*

In the ETOGAS process, hydrogen is generated using alkaline pressurised electrolysis. The system is based on dynamic, intermittent operation of photovoltaic cells linked to the electrolysers. CO_2 methanation is accomplished using a parallel plate fixed bed reactor system using nickel catalyst (Zhu 2018). The first incarnation of the ETOGAS process was a 6 MWe plant that was constructed for German automotive manufacturer Audi AG in Werlte, Germany, shown in Figure 95 below.

***Figure 95:** Audi e-Gas plant*[187]

The Audi e-Gas plant, operational since 2013, uses wind power and CO_2 from a biogas plant. The e-Gas plant was built to provide a source of renewable SNG to fuel Audi's g-tron line of vehicles, which are fitted with engines that run on compressed natural gas.[188]

In 2016, the Swiss clean-tech company Hitachi Zosen Inova (HZI) acquired ETOGAS to form HZI EtoGas. In 2017, the Japanese R&D organisation, New Energy and Industrial Technology Development Organization (NEDO), awarded a contract to HZI to construct a power-to-gas plant using CO_2 from the INPEX Koshijihara coal-fired thermal power station in Nagaoka, Niigata Prefecture. The plant included a proton exchange membrane (PEM) electrolyser to produce hydrogen from electricity and water.[189] The plant was successfully commissioned in October 2019.[190]

In 2022, another e-gas plant, owned by Energie Steiermark, started operation in Gabersdorf, Austria using the ETOGAS process. A 1 MW PEM electrolyser driven by solar power is used to produce 40 Nm^3/h hydrogen which is reacted with CO_2 from a biogas plant. The system produces 21.5 Nm^3/h methane which is fed into the grid.[191]

HZI EtoGas currently offers commercial installations of the ETOGAS process in sizes from 8 to 500 m^3 of product gas per hour.

8.3.8.2 Victorian Research Context

CSIRO is developing improved catalysts and reactors for CO_2 hydrogenation processes, particularly for CO_2 methanation. The catalyst development work considers both thermal and photo-catalysis

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[187] https://www.audi.com.au/au/web/en/models/layer/technology/g-tron/power-to-gas-plant.html
[188] https://www.audi.com.au/au/web/en/models/layer/technology/g-tron.html
[189] https://www.inpex.co.jp/english/news/assets/pdf/e20191016.pdf
[190] https://www.hz-inova.com/hzc-and-hzi-realise-first-joint-power-to-gas-project/
[191] https://www.hz-inova.com/projects/gabersdorf-aut/

facilitated by high-throughput techniques to screen and validate the activity of several of materials. CSIRO's research activities also include the development of new reactor designs for real-time optimisation of CO_2 recycle reactions.

CSIRO has developed a catalyst that is highly active and stable, derived from a Ru-impregnated zirconium-based metal–organic framework (MOF) material. To make the catalyst, the Ru-doped MOF is transformed, under reaction conditions, into a catalytic mixture of Ru-nanoparticles supported on monoclinic and tetragonal ZrO_2 nanoparticles. The catalyst has been shown to yield CO_2 conversions from syngas (H_2: CO_2 = 4: 1) of 96 % and a CH_4 selectivity of 99 % (Lippi et al. 2017; Lippi et al. 2021).

CSIRO has capability and expertise in formulating, synthesising and testing a range of catalysts. It has expertise in a range of techniques for catalyst formulation, including impregnation, coating and co-precipitation. CSIRO has the capacity to undertake high throughput catalyst assessment, and has a purpose-built prototype or pilot scale testing facility at Clayton.

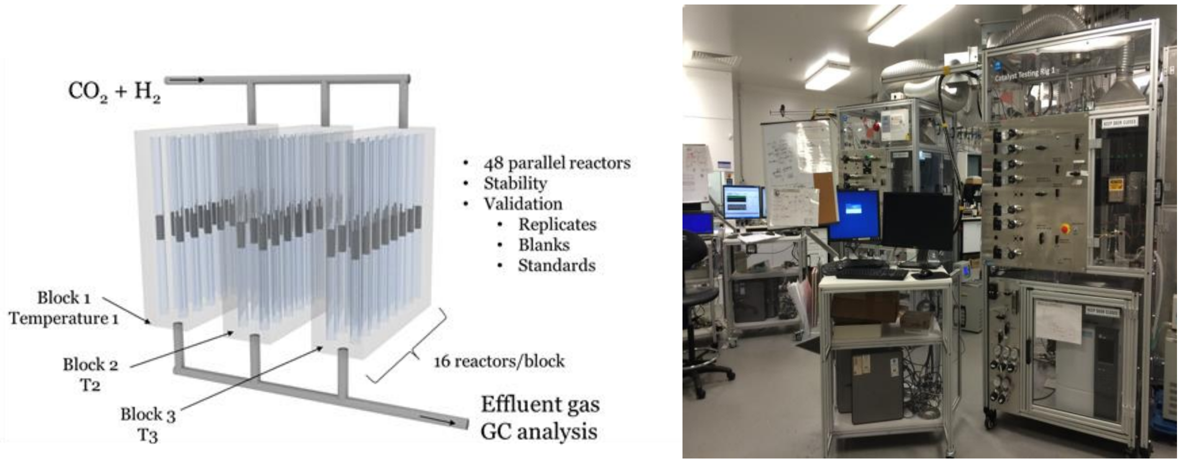

Figure 96: *Multi-channel high throughput catalyst testing and lab scale catalyst testing rig at CSIRO*

These technologies are estimated to be at TRL 2 – i.e. proven at lab scale using high throughput catalyst testing facility at CSIRO. Further opportunity for up-scaling the catalyst is being sought.

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8.3.8.3 ACI Comments

The rising cost of natural gas is putting pressure on the cost-competitiveness of Victorian manufacturing companies. There is strong international interest in recycling CO_2 *to methane, based on the fact that it can help to reduce net* CO_2 *emissions. An example of this is Audi's g-tron line of automobiles, which are designed to run on low-emissions synthetic natural gas.*

However, for this to make sense, the hydrogen must be produced from renewable sources. It is currently unclear whether that will be possible at sufficient scale in Victoria for the produced methane to be cost-competitive.

While recycling CO_2 *to methane is doubtless a topic of great interest overseas, ACI does not recommend a significant R&D involvement until the economics of the process are more clearly understood. Fundamental work, such as that being done at CSIRO, can assist with this.*

8.3.9 Graphene

8.3.9.1 Current Status

Graphene is the name given to a two-dimensional monolayer sheet of sp^2-hybridized carbon arranged in a honeycomb network, representing a single layer of a graphite structure. The molecular structure of graphene (see Figure 97 below) is the basic structural element of other allotropes, including carbon nanotubes, fullerenes and graphene quantum dots. Graphene is chemically inert and stable, behaves as an impermeable membrane, and conducts heat and electricity better than any metal. In proportion to its thickness, graphene is about 100 times stronger than the strongest steel. Graphene is nearly transparent and yet has the ability to sustain extremely high densities of electric current (a million times higher than copper), offering potential for use in transparent electronic devices (Novoselov et al. 2012).

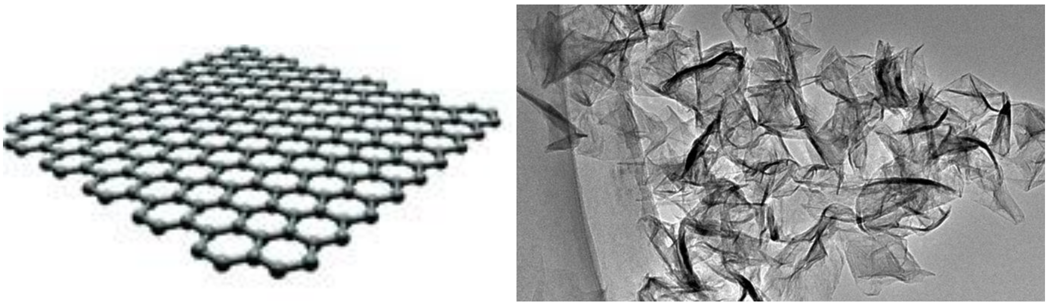

Figure 97: *Graphene molecular structure and transmission electron microscopy image* [192]

The large-scale industrial use of graphene will require large scale and cost-effective production methods, balancing ease of fabrication and final material quality with the properties required for

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[192] https://www.nature.com/articles/d41586-018-06103-y

specific applications. Given that graphite is relatively inexpensive and available in large quantities, the method that has received the most attention for large-scale production of graphene is the ‘top-down’ method, i.e., splitting graphite into individual sheets either mechanically or chemically. The main technique used commercially, known as Hummers’ method, involves chemical modification of graphite using potassium permanganate and sulphuric acid to produce a water dispersible intermediary, graphite oxide, which is exfoliated to graphene oxide through addition of mechanical energy. Subsequent deoxygenation, by thermal annealing or through treatment with chemical reducing agents, transforms graphene oxide to graphene (Allen et al. 2009).

A new ‘bottom-up’ method that has recently been introduced involves growing graphene monolayers on the surface of liquid metals at low temperature. Liquid metals are an ideal substrate for crystal growth on their surface since they can naturally establish a smooth, soft, defect and stress-free interface. Since the metal beneath the surface layer is a non-polar liquid, attractive forces between the parent metal and the surface compound are weak and localised. As a result, delamination and exfoliation of the surface layer is easily achieved (Daeneke et al. 2018).

For example, researchers at Wuhan University in China have demonstrated the feasibility of fabricating uniform sheets of graphene on the surface of GaCu liquid metal alloys at 800 °C by atmospheric chemical vapour deposition using CH_4 as the carbon source (Wang et al. 2016c).

8.3.9.2 Victorian Research Context

Researchers at RMIT University fortuitously discovered that sheets of graphene can be synthesised by bubbling CO_2 through a column of 75 wt.% gallium – 25 wt.% iridium liquid metal at atmospheric pressure and 100-400 °C temperature (Daeneke et al. 2023), as shown in Figure 98 below. This is a remarkably simple process for converting CO_2 to graphene, without the use of a supplementary reductant such as hydrogen.

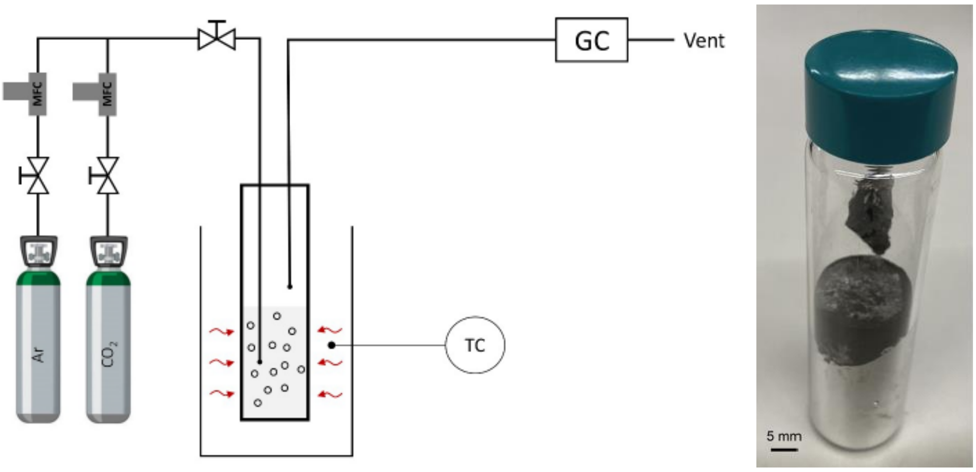

Figure 98: *Schematic of experimental liquid metal bubbling column reactor, and an image of the carbon product accumulated above the liquid metal after* CO_2 *decomposition at 200°C for 4 hours (Zuraiqi et al. 2022).*

It has been found that CO_2 spontaneously interacts with Ga atoms, resulting in cleavage of C-O bonds and formation of gallium oxide, Ga_2O_3:

$$3\ CO_2 + 4\ Ga \rightarrow 2\ Ga_2O_3 + 3\ C$$

Pure carbon, in the form of microscopic sheets of graphene, floats to the surface of the liquid. The iridium component is inert to CO_2, but serves to reduce the melting temperature of the mixture to 15^{o}C, so it is liquid at room temperature. Production of graphene proceeds slowly at room temperature, but increases with increasing temperature up to 400^{o}C, at which point CO begins to form. Production of graphene is strongly exothermic, so the heat required to sustain the process is self-generated (Zuraiqi et al. 2022).

Gallium is used commercially in production of gallium arsenide wafers for the electronics industry. Gallium is mostly obtained as a by-product of aluminum refining and, to lesser extent, of refining of zinc (Moskalyk 2003). China produces around 80% of the world's gallium, exporting 94 tonnes in 2022. Small amounts of gallium - around 10 tonnes in 2021 - are produced by Japan, Russia and South Korea, with small amounts also coming from recycled material.[193] The global market was worth US$1.9 billion in 2022, and is expected to reach US$17 billion by 2032, growing at 24.5% p.a.[194]

During the processing of bauxite to alumina in the Bayer process, gallium oxide accumulates in the sodium hydroxide liquor. Crude gallium is recovered using ion-exchange resin and then converted to gallium metal by electrolysis (Moskalyk 2003). Similarly, the RMIT researchers have demonstrated proof-of-concept of electrolysis for recycling the gallium oxide by-product to gallium metal (Zuraiqi et al. 2022).

Currently, the RMIT process is operated using 20-60 ml liquid metal in a 2 litre reactor, with about 5% CO_2 conversion efficiency. The research emphasis is on improving the reaction kinetics through increased gas-liquid contact, as support for construction of a large lab-scale reactor system. There is still a large amount of work to be done to devise an effective gas-liquid contacting system for efficient CO_2 conversion, recovery and separation of graphene and gallium oxide, and recycling of gallium oxide to gallium metal. As such, this technology is still only at TRL 1-2.

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[193] https://www.reuters.com/markets/commodities/where-are-strategic-materials-germanium-gallium-produced-2023-07-04/
[194] https://www.persistencemarketresearch.com/market-research/gallium-market.asp

9 Electrochemical Conversion of CO_2

This section discusses processes for recycle of CO_2 that use a combination of electrical energy and catalysis to electrochemically convert CO_2 into value-added products. Progress in the electrochemical conversion of CO_2 to syngas, formic acid and carbon nanofibres is described.

Before this, a brief overview is given on the electrolysis technologies that are available for using renewable energy to split water to hydrogen and oxygen. Electrochemical reaction systems are predominantly modifications of these basic design concepts, so this will serve as a helpful introduction.

9.1 HYDROGEN PRODUCTION BY ELECTROLYSIS

9.1.1.1 Current Status

A key element for the successful recycling of CO_2 into useful products in an environmentally sustainable way is the availability of low cost CO_2-free hydrogen. In the scientific literature, it is assumed that such hydrogen will be generated from renewable energy using electrolysis to split water into hydrogen to oxygen. Certainly, electrolysis has a role to play in converting intermittent renewable energy into a stable chemical form, using hydrogen as a form of chemical battery. The potential for using the hydrogen to convert recycled CO_2 into value-added is very much dependent on the economies of scale that can be achieved using electrolysis (and other electrochemical processes, as discussed later).

In 2015, the worldwide production of hydrogen was around 50 Mt/y, mostly from fossil fuels (steam re-forming of natural gas, coal gasification, partial oxidation of hydrocarbons), while hydrogen production via electrolysis using renewable energy sources amounts accounted for only 4 % (Sapountzi et al. 2017). The proportion of hydrogen produced by electrolysis will certainly grow at a rapid rate in the near future, in line with increasing deployment of renewable energy.

Depending on the kind of electrolyte and the operating temperature, water electrolysers are classified into three main categories: alkaline, polymer–electrolyte membrane (PEM) and solid oxide electrolysers (SOE). The operating principles of are illustrated in Figure 99 below.

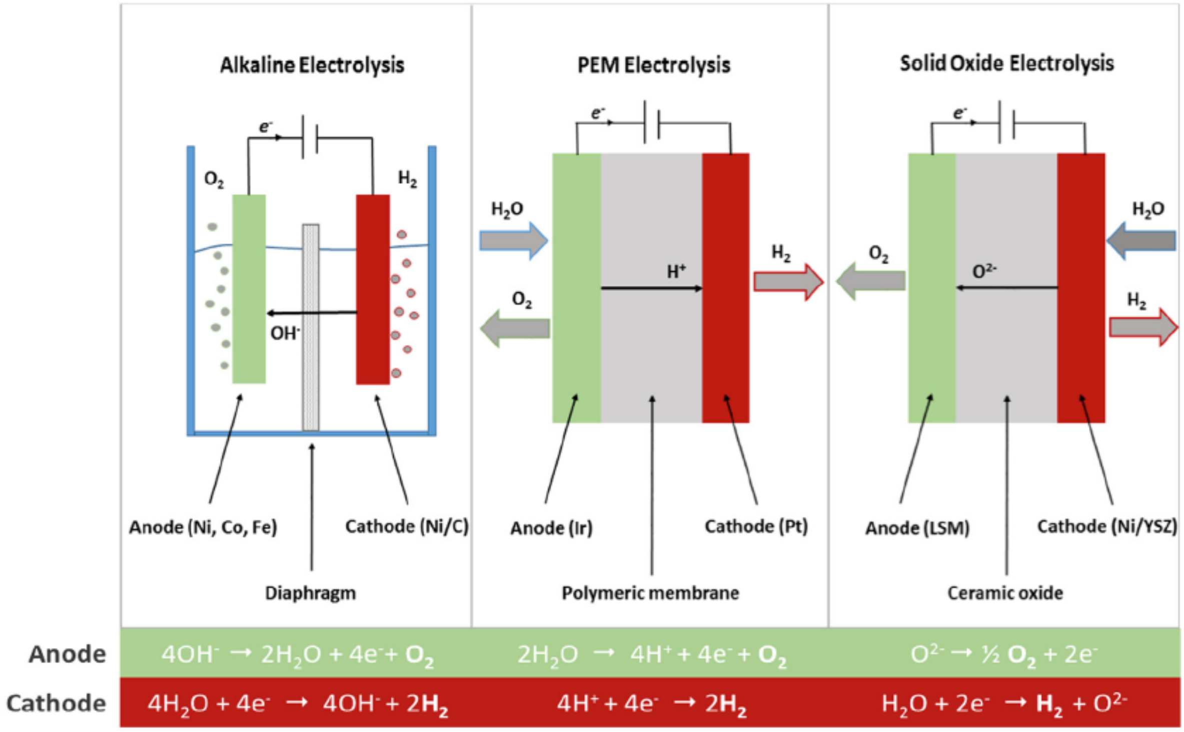


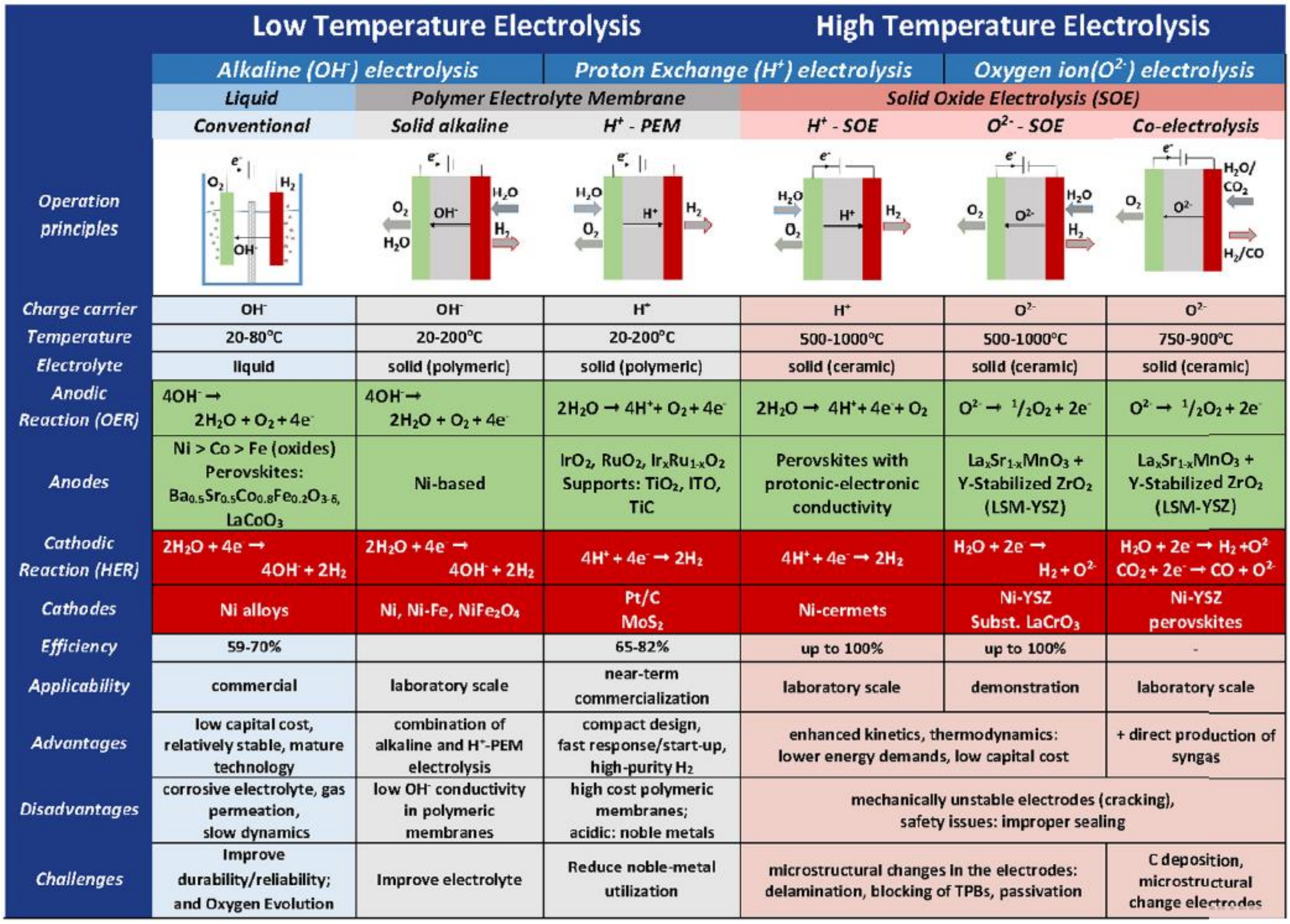
Figure 99: *Operating principles of principles of alkaline, PEM and SOE water electrolysis (Sapountzi et al. 2017)*

Alkaline electrolysers operate at low temperatures (typically below 100°C) under alkaline water conditions. This is the simplest and most mature of the three electrolysis technologies. Alkaline electrolysis is well established as a commercial technology, with suppliers such as De Nora SAP, Norsk Hydro, Electrolyzer Corp, Teledyne Energy Systems, General Electric and Siemens. The main advantages of alkaline electrolysis are its relatively low cost, due to the use of non-noble electrodes and its long-term stability (Sapountzi et al. 2017).

PEM electrolysers also operate in the low temperature range. The use of solid polymeric membranes with protonic conductivity for water electrolysis is advantageous as it allows for compact, robust and stackable cell designs with minor safety issues. However, the acidic environment in PEM electrolysers requires the use of using expensive noble metal catalysts which, along with the high cost of polymeric membranes, has hindered the commercialisation of this technology (Sapountzi et al. 2017).

SOE electrolysers typically operate at temperatures above 500 °C, with water in the form of steam. High temperature steam water electrolysis can provide high efficiency, with lower total cost compared to alkaline electrolysis due to favourable thermodynamics and kinetics. As a result of their high operating temperatures, SOE electrolysers high temperature offers the possibility for co-electrolysis of water and CO_2 mixtures for the production of syngas, which can be further converted to methanol or higher hydrocarbons. However, the high temperature is also the source of degradation and lack of stability, which have to be solved before SOE can be commercialised on a large scale (Sapountzi et al. 2017).

The relative advantages and disadvantages of each type of electrolysis technology are summarised in Figure 100 below.



	Low Temperature Electrolysis			High Temperature Electrolysis		
	Alkaline (OH^-) electrolysis		Proton Exchange (H^+) electrolysis		Oxygen ion(O^{2-}) electrolysis	
	Liquid	Polymer Electrolyte Membrane		Solid Oxide Electrolysis (SOE)		
	Conventional	Solid alkaline	H^+ - PEM	H^+ - SOE	O^{2-} - SOE	Co-electrolysis
Operation principles	e^-, O_2, H_2, OH^-	e^-, O_2, H_2O, OH^-, H_2O, H_2	e^-, H_2O, O_2, H^+, H_2	e^-, H_2O, O_2, H^+, H_2	e^-, O_2, O^{2-}, H_2O, H_2	e^-, O_2, O^{2-}, H_2O/CO_2, H_2/CO
Charge carrier	OH^-	OH^-	H^+	H^+	O^{2-}	O^{2-}
Temperature	20-80°C	20-200°C	20-200°C	500-1000°C	500-1000°C	750-900°C
Electrolyte	liquid	solid (polymeric)	solid (polymeric)	solid (ceramic)	solid (ceramic)	solid (ceramic)
Anodic Reaction (OER)	$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$	$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$	$2H_2O \rightarrow 4H^+ + O_2 + 4e^-$	$2H_2O \rightarrow 4H^+ + 4e^- + O_2$	$O^{2-} \rightarrow {}^1/_2O_2 + 2e^-$	$O^{2-} \rightarrow {}^1/_2O_2 + 2e^-$
Anodes	Ni > Co > Fe (oxides) Perovskites: $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$, $LaCoO_3$	Ni-based	IrO_2, RuO_2, $Ir_xRu_{1-x}O_2$ Supports: TiO_2, ITO, TiC	Perovskites with protonic-electronic conductivity	$La_xSr_{1-x}MnO_3$ + Y-Stabilized ZrO_2 (LSM-YSZ)	$La_xSr_{1-x}MnO_3$ + Y-Stabilized ZrO_2 (LSM-YSZ)
Cathodic Reaction (HER)	$2H_2O + 4e^- \rightarrow 4OH^- + 2H_2$	$2H_2O + 4e^- \rightarrow 4OH^- + 2H_2$	$4H^+ + 4e^- \rightarrow 2H_2$	$4H^+ + 4e^- \rightarrow 2H_2$	$H_2O + 2e^- \rightarrow H_2 + O^{2-}$	$H_2O + 2e^- \rightarrow H_2 + O^{2}$ $CO_2 + 2e^- \rightarrow CO + O^{2-}$
Cathodes	Ni alloys	Ni, Ni-Fe, $NiFe_2O_4$	Pt/C MoS_2	Ni-cermets	Ni-YSZ Subst. $LaCrO_3$	Ni-YSZ perovskites
Efficiency	59-70%		65-82%	up to 100%	up to 100%	-
Applicability	commercial	laboratory scale	near-term commercialization	laboratory scale	demonstration	laboratory scale
Advantages	low capital cost, relatively stable, mature technology	combination of alkaline and H^+-PEM electrolysis	compact design, fast response/start-up, high-purity H_2	enhanced kinetics, thermodynamics: lower energy demands, low capital cost		+ direct production of syngas
Disadvantages	corrosive electrolyte, gas permeation, slow dynamics	low OH^- conductivity in polymeric membranes	high cost polymeric membranes; acidic: noble metals	mechanically unstable electrodes (cracking), safety issues: improper sealing		
Challenges	Improve durability/reliability; and Oxygen Evolution	Improve electrolyte	Reduce noble-metal utilization	microstructural changes in the electrodes: delamination, blocking of TPBs, passivation		C deposition, microstructural change electrodes

Figure 100: *Typical characteristics of the main electrolysis technologies (Sapountzi et al. 2017)*

A thorough review of the current status of development of electrolysis technologies for hydrogen production is available (Sapountzi et al. 2017).

As discussed in Section 8.3.5 above, Carbon Recycling International (CRI) operates a pilot plant in Iceland that produces 4,000 t/y methanol using recycled CO_2 and hydrogen produced using renewable energy and alkaline electrolysis. From 2014 to 2019, CRI and its consortium partners were involved in the MefCO_2 project, which was a pilot-scale demonstration of CO_2-to-methanol at RWE Power's Coal Innovation Centre in Niederaußem, Germany. The methanol plant had a production capacity of 1 ton of methanol per day, using 1.37 ton of CO_2 (captured from the Niederaußem lignite-fired power station) and 0.19 ton H_2 (produced using PEM electrolysis using wind energy).[195]

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[195] https://www.rwe.com/en/research-and-development/rwe-innovation-centre/e-fuels/mefco2/

In January 2018, Shell and ITM Power began collaboration on the REFHYNE project, which involved installation of a 10 MW PEM electrolyser – the largest in the world – at Shells's Rhineland refinery, in Wesseling, Germany. Currently the Rheinland refinery, Germany's largest, requires approximately 180,000 t/y of hydrogen, which is produced by steam reforming of natural gas. The PEM electrolyser was fully integrated into the refinery processes and produced an additional 1,300 t/y of hydrogen using renewable energy.[196] The electrolyser (shown in Figure 101 below), came on-line in July 2021.

Figure 101: *Europe's largest PEM hydrogen electrolyser at Rheinland refinery*[197]

In October 2021, the REFYHNE II consortium secured €32.4 million from the European Climate, Infrastructure and Environment Executive Agency (CINEA) to develop a 100MW electrolyser at the Shell Energy and Chemicals Park. The project is coordinated by SINTEF and, as well as Shell and ITM Power, phase two includes project partners: Linde Engineering, ITM Linde Electrolysis, Fundacion Tecnalia Research & Innovation, Element Energy, and Concawe.[198]

The current leading company in SOE technology is Sunfire GmbH of Germany. Its Sunfire-Hylink electrolysers are available in 150 kW modules, each capable of producing up to 40 Nm^3/h hydrogen. The modules can be delivered in containerised form, with each container capable of producing 200 Nm^3/h hydrogen from 750 kW$_{AC}$ electricity.[199]

9.1.1.2 Victorian Research Context

Research on electrolysis system design is currently under way at CSIRO in Clayton, at the Centre for Hybrid Energy Systems.[200] This work is focused on reducing the cost of electrolysis through improved engineering design and direct coupling with solar PV, to produce an integrated package.

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[196] http://www.itm-power.com/news-item/worlds-largest-hydrogen-electrolysis-in-shells-rhineland-refinery

[197] https://www.powermag.com/shell-starts-up-10-mw-refhyne-hydrogen-electrolyzer-eyes-expansion-to-100-mw/

[198] https://itm-power.com/projects/refhyne

[199] https://www.sunfire.de/en/products-and-technology/sunfire-hylink

[200] https://www.csiro.au/en/Do-business/Services/Materials-infrastructure/CHES

In 2018, the CSIRO National Hydrogen Roadmap study concluded that the most cost-effective way to produce CO_2-free hydrogen in Victoria in 2030, at the scale needed for export to the Japanese market, would be by gasification of lignite and geosequestration of the produced CO_2.[201]

9.1.1.3 ACI Comments

The development of improved electrolysis technology for hydrogen generation is currently an area of active research by major international companies. While CSIRO has excellent capabilities in this area, ACI does not recommend hydrogen production by electrolysis as a significant research topic.

9.2 SYNGAS PRODUCTION BY ELECTROLYSIS

9.2.1.1 Current Status

Syngas (synthesis gas, predominantly CO and H_2) is a commonly used feedstock for production of chemicals and liquid fuels. Syngas is traditionally produced via coal gasification or steam reforming of natural gas.

This section describes two technological routes that are being developed to upgrade CO_2 to reactive CO using electrolysis. The first involves co-electrolysis of steam and CO_2 to produce syngas in a high temperature SOEC reactor. The second involves low temperature direct electrolytic reduction of CO_2.

9.2.1.1.1 High temperature co-electrolysis of steam and CO_2

Co-electrolysis of steam and carbon dioxide ($H_2O + CO_2 \rightarrow H_2 + CO + O_2$) using renewable energy sources is being developed as an alternative route for producing synthesis gas without consuming fossil fuels or emitting greenhouse gases.

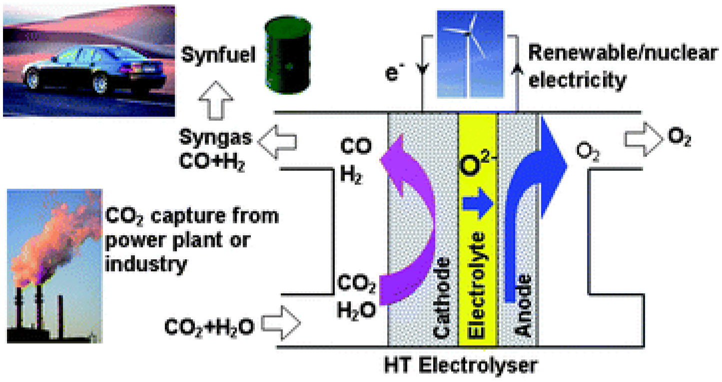

Figure 102: *Conceptual scheme for syngas by co-electrolysis (Fu et al. 2010)*

Sunfire GmbH, Germany, has led the development of industrial co-electrolysis equipment. Its Sunfire-SynLink co-electrolyser is based on SOE technology (Rüger 2018). Since 2015, Sunfire has operated a 10 kW electrolyser pilot plant in Dresden, where the produced syngas was converted to diesel fuel

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[201] https://www.csiro.au/en/Do-business/Futures/Reports/Hydrogen-Roadmap

using Fischer-Tropsch synthesis. The pilot plant was operated continuously for more than 1500 hours and reached a carbon conversion efficiency of 90 %.[202] The Sunfire process is currently available commercially as Sunfire-SynLink SOEC.[203]

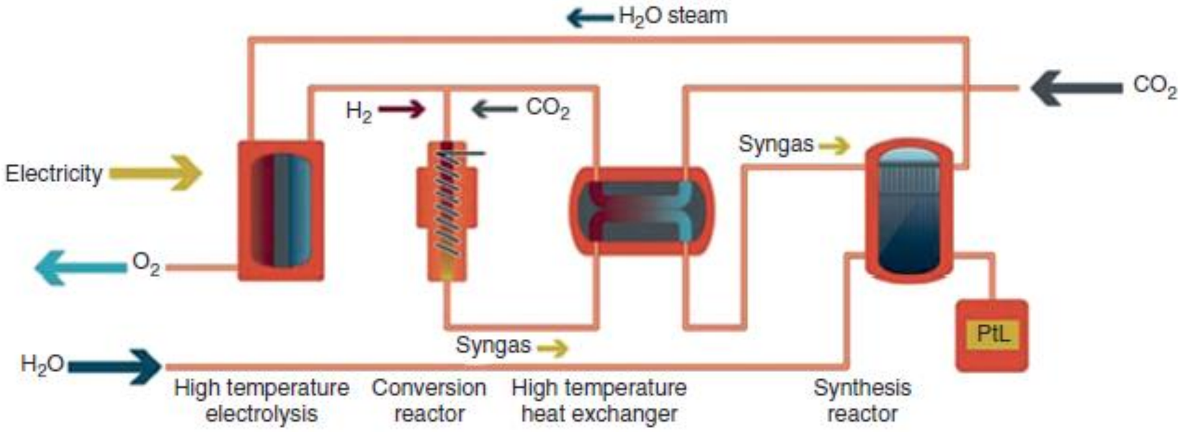

Figure 103: *Production of Blue Crude using syngas from co-electrolysis of CO_2 and steam (Zhu 2018)*

The Sunfire-SynLink SOEC will form part of a demonstration CO_2-to-gasoline plant being built by Norsk e-Fuel in Mosjøen, Norway. The syngas will be converted to crude oil using Fischer-Tropsch synthesis, and subsequently upgraded to aviation fuel. The goal is to start production as early as 2026.[204]

9.2.1.1.2 Low temperature CO_2 electrolysis

9.2.1.1.2.1 Siemens process

In Germany, as part of the Kopernikus project P2X, Siemens is developing a membrane system for the direct electrochemical reduction of CO_2 (CO_2-RR) using industrially-available equipment. The principle of the system is illustrated in Figure 104 below.

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[202] https://www.sunfire.de/en/company/news/detail/first-commercial-plant-for-the-production-of-blue-crude-planned-in-norway
[203] https://www.sunfire.de/en/syngas
[204] https://www.norsk-e-fuel.com

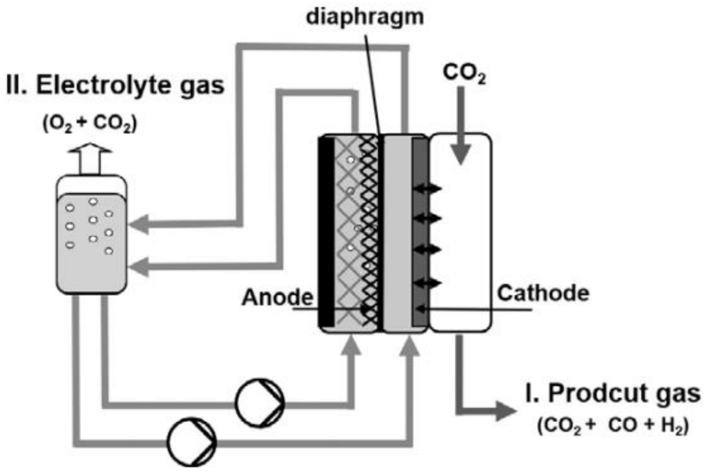

***Figure 104:**: Siemens CO_2-to-CO electrolysis system (Krause et al. 2020)*

Both the anode and cathode are silver-based gas diffusion electrodes (GDE), which are commercially used in chlorine alkaline electrolysis. CO_2 is reduced at the cathode to produce CO:

$$CO_2 + H_2O + 2\ e^- \rightarrow CO + 2\ OH^-$$

Oxygen is evolved at the anode:

$$H_2O + 2\ e^- \rightarrow 0{:}5\ O_2 + 2\ H^+$$

The protons evolved at the anode are neutralised by bicarbonate or carbonate in the electolyte, evolving CO_2 as a side-reaction:

$$H^- + HCO_3- \rightarrow CO_2 + H_2O \quad \text{or} \quad CO_3^{2-} + 2\ H^- \rightarrow CO_2 + H_2O$$

The anolyte and catholyte are mixed after passing through the half-cells to avoid accumulation of charge on either electrode, and to ensure equilibration of cations, protons and anions.

To date, the system has been scaled up to an active area of 300 cm^2. The system demonstrated current density up to 300 mA cm^{-2}, faradaic selectivity above 90 %, CO concentration in product gas above 30 %, at an operating temperature of 60 ^oC. Stable operation was observed over a period of 600 hours, and testing is ongoing to demonstrate endurance in the range of thousands of hours. Further scaling will be part of Kopernikus P2X phase II (Krause et al. 2020).

9.2.1.1.2.2 Dioxide Materials process

In the United States, Dioxide Materials Inc. is collaborating with membrane manufacturer 3M Company to develop electrochemical processes for producing syngas and formic acid, two products that have been shown to be economically viable for CO_2 electrolysis (Jouny et al. 2018). This work is based on overcoming the technical challenges associated with PEM electrolysers.

While significant technical progress has been made in the development of acidic PEM electrolysers, a key barrier is the need to use platinum catalysts for the reactions, which are both costly and limited in supply. The alternative path being followed by Dioxide Materials and 3M Company is to develop alkaline membranes that have the potential to both eliminate the need for expensive catalysts, and also be produced at lower cost and volumes.

The 3M Company has developed a new anion exchange membrane (AEM) technology, known as Sustainion™, with widespread applications in fuel cells, electrolysers, and flow batteries. Electrolysers using Sustainion™ membranes have achieved power densities in excess of 50 W/cm^2 using only 0.25mg/cm^2 of IrO_2 as the anode catalyst. In comparison, present PEM electrolysers typically use loadings of 4-8 mg/cm^2 of Platinum Group Metal and achieve much lower power densities (Liu et al. 2016).

Dioxide Materials has developed a CO_2 electrolyser capable of efficiently producing CO at high selectivities. The CO_2 cell consists of a two-compartment design utilizing the alkaline stable anion exchange membrane to separate the anode and cathode compartments. Humidified CO_2 is fed to the cathode while water with some electrolyte is circulated through the anode, as indicated in Figure 103. CO_2 reacts with water on the cathode via the reaction:

$$CO_2 + H_2O + 2\ e^- \rightarrow CO + 2OH^-$$

the OH^- crosses through the membrane to the anode where it reacts via the reaction

$$2OH^- \rightarrow H_2O + \tfrac{1}{2}\ O_2 + 2\ e^-$$

The net reaction is: $CO_2 \rightarrow CO + \tfrac{1}{2}\ O_2$

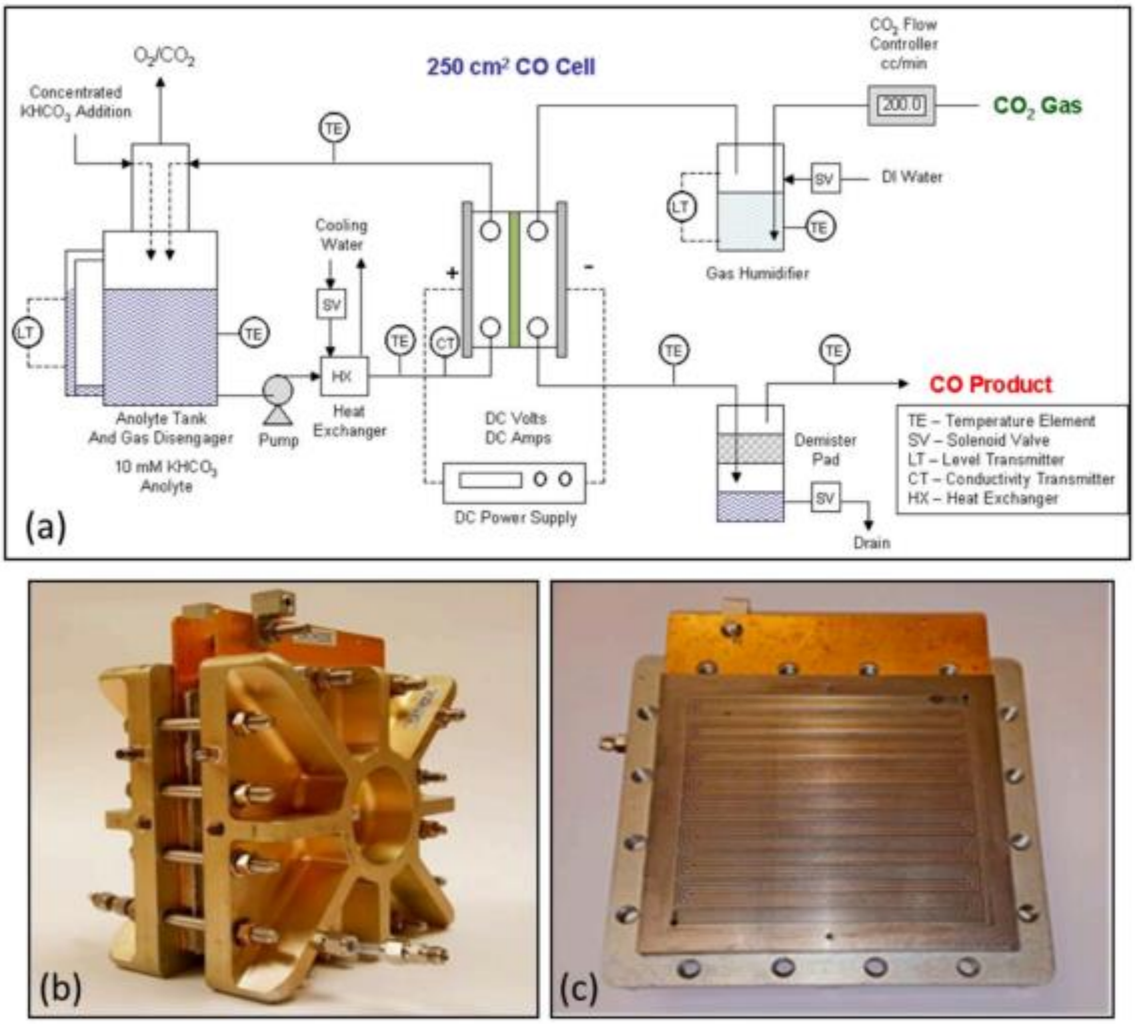

Figure 105: *Schematic of the 250 cm^2 CO_2 cell experimental test system is shown in (a). The DM modified 250 cm^2 CO_2 electrolyser cell as shown in (b) on the left. The design used a titanium serpentine anode flow field design as shown in (c) (Kaczur et al. 2018)*

The anode consists of a nanoparticle IrO_2 catalyst on a GDE structure, and the cathode is a GDE utilizing a nanoparticle Ag/imidazolium-based ionomer catalyst combination. The CO_2 cell has been scaled up to 250 cm^2 area, and operated at current densities of 200 to 600 mA/cm^2 at voltages of 3.0 to 3.2 respectively, with CO_2 to CO conversion selectivity of 95–99%. The power consumption was calculated to be 5.8 DC kWh/kg of CO (Kaczur et al. 2018).

Dioxide Materials is working with industrial partners to scale up the CO_2 cell. Development work is also focussed on finding suitable stable non-precious metal catalyst replacements for the nanoparticle IrO_2 used in the anode (Kaczur et al. 2018).

9.2.1.2 Victorian Research Context

CSIRO is developing a novel technology which converts CO_2 generated from industrial processes such as fertilizer production, cement manufacturing, synthetic chemical production and coal fired power plants, into high value fuels and chemicals (methanol, gasoline, jet and diesel, lubricants) using renewable energy and/or by using excess electricity.

The project will be delivered by a CSIRO-led consortium with RayGen Resources Ltd. (Australia), ADME fuels Ltd. (Australia), Ben Gurion University at Negev (Israel), Johnson Matthey (UK), and Northwestern University in USA. The project is being run as four parallel programs with each partner focusing on different aspects of technology with CSIRO as lead.

The technology being developed is based upon solid oxide electrolysis (SOE), which electrochemically converts mixture of CO_2 and steam into a mixture of H_2 and CO (syngas), which can be then converted into transportable liquid/gaseous fuels using suitable downstream fuel synthesis process integrated to SOE reactor. The downstream processes are highly exothermic, and as such heat required for endothermic SOE operation can be obtained via by integration of two reactors. Additionally, heat from solar thermal or waste heat from industrial process can be incorporated to boost efficiency further.

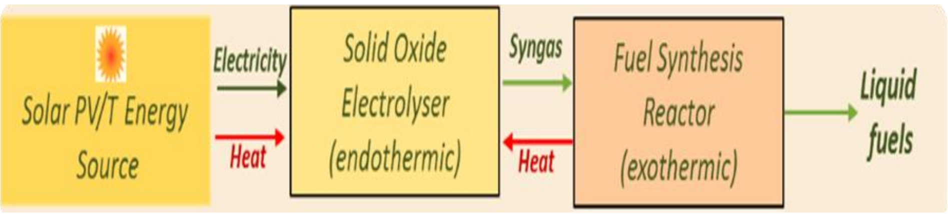

Figure 106: *CSIRO liquid fuel synthesis from CO_2 using Solid Oxide Electrolyser*

Since solar PV/thermal systems and downstream fuel synthesis reactors are at a more advanced stage of development than the novel tubular SOE cell and stacks, the major focus of this research is on SOE materials development and building a scaled-up SOE stack at CSIRO's Clayton labs. The inexpensive and robust ceramic electrodes developed by CSIRO avoid the limitations associated with conventional nickel-based electrodes. Further, a patented iron spinel catalyst, developed at Ben Gurion University for downstream processing, operates over a wide range of CO-to-H_2 ratios (as opposed to H_2 rich syngas), giving flexibility to SOE operation to maximise its efficiency.

Preliminary experiments have demonstrated proof of concept. In the fuel synthesis reactor, CO conversion was 82% while C5+ selectivity of the combined CO conversion and oligomerization processes was 79%. Stable operation for 4000 h was demonstrated, with an overall energy efficiency of 67% (Kulkarni et al. 2021).

The long-term goals of this work are to demonstrate a fully integrated system consisting of Solar Energy Source coupled directly to SOE, and a thermally integrated catalytic reactor for downstream processing of synthesis gas to produce liquid fuels. Challenges remaining to be addressed include: inefficient electrode materials design and lifetime, lack of real system data on SOE coupled to solar PV system and economical method for downstream processing.

A direct involvement of commercial companies with a firsthand experience in solar energy deployment and renewable fuels markets is desirable, as this would enable development of a realistic commercialisation roadmap. The information valuable for commercialisation of the technology will be safeguarded, and integrated within the business plans for distribution amongst potential investors to establish a spin-off or technology licensing around this technology. CSIRO anticipates the technology would be in pre-commercialisation stage (TRL 6) in three years.

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9.2.1.3 ACI Comments

Catalytic reduction of CO_2 using SOE technology is the most prospective approach for upgrading renewable energy to valuable chemicals. This is because SOE operates at the high temperatures needed to overcome the energy barrier to CO_2 conversion.

CSIRO has a lot of credibility in this field, having successfully commercialised a solid oxide fuel cell system called BlueGen,[205] which generates electricity and heat from natural gas. CSIRO currently has a range of projects under development around Solid Oxide Electrolyser technology, produce syngas and further upgrading to methane, methanol, fuels, etc. This is a highly specialised area, and CSIRO has established an excellent facility and technical capabilities. Currently the TRL level is about 4.

Solid Oxide Electrolyser technology allows renewable energy to be effectively harnessed to recycle CO_2 into a range of high value products. The SOE technology can be employed in two different ways. One is for production of syngas for catalytic conversion of CO_2 to useful chemicals and fuels, such as methane and methanol. The second is for production of ethanol using LanzaTech's gas fermentation process (Section 6.3.2.1.1). This is likely to be a more economical route to ethanol production, compared with syngas production by gasification, which requires high throughput to achieve economies of scale. ***ACI recommends support for further development and scale up of this technology to TRL 6 and beyond, to serve as a platform for the development of higher value products such as methane, methanol and ethanol.***

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[205] http://www.solidpower.com/en/bluegen/

9.3 FORMIC ACID PRODUCTION BY ELECTROLYSIS

9.3.1.1 Current Status

Among all of products from CO_2 electrolysis, formic acid is one of the highest value-added chemicals that can be produced from CO_2 reduction. The price for formic acid is around US$1300 per ton, which is approximately the same as that of carbon monoxide, but much higher than that for methanol and ethylene (Du et al. 2017).

A few excellent review articles have reported on the electrolysis of CO_2 in terms of the catalyst (Zhu et al 2016) and the conversion towards formic acid with regard to the aspects of reaction mechanisms (Chaplin & Wragg 2003) engineering, and economic feasibility (Agarwal et al. 2011). Good reviews on development of electrochemical reduction of CO_2 to formic acid, in terms of electrode structure, catalyst materials, electrolyte, and cell design are available (Lu et al. 2014; Du et al. 2017).

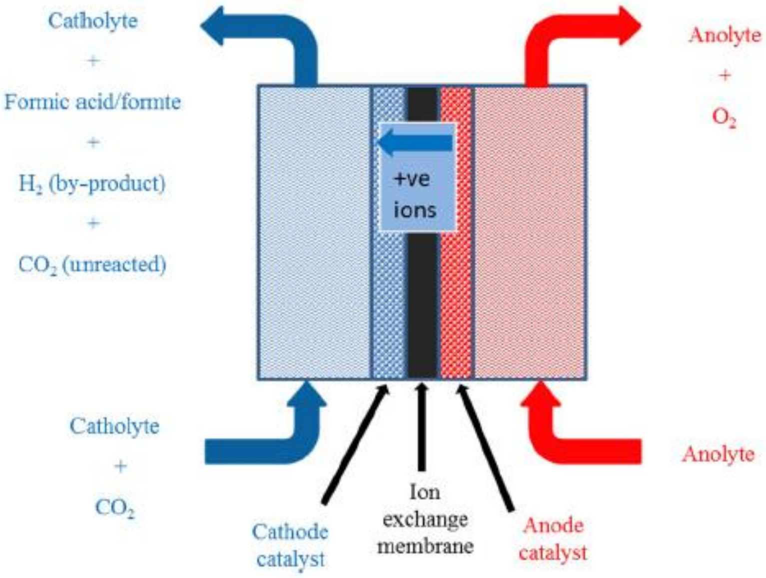

Figure 107: *Schematic diagram of electrolysis of CO_2 to formic acid (Du et al. 2017).*

The literature suggests that electrochemical conversion of CO_2 to formic acid or formate is still at an early stage with many issues that need to be solved. Three companies currently investigating the electrolysis of CO_2 to formic acid and other products are DNV GL (Rode et al. 2016) and Avantium (Schouten & Gruter 2017) in the Netherlands, and Dioxide Materials in the U. S. (Kaczur et al. 2018).

Norwegian company DNV GL developed the ECFORM process to convert CO_2 into formic acid and formate salts directly, using a proprietary tin-based alloy catalyst as cathode. DNV GL built a semi-pilot ECFORM demonstration reactor with a 600 cm^2 surface area and a capacity of reducing approximately 1 kg CO_2/day. However, significant technological advancements are needed before large-scale production can take place (Zhu 2019).

Dioxide Materials' CO_2 electrolyser is still at an early stage of development, with an emphasis on demonstrating efficiency and long-term stability. A series of trials at 5 cm^2 scale demonstrated that formic acid could be produced at 2.4M concentration for more than 1000 hours, with faradic efficiency around 70%. Similar performance was achieved using a simulated flue gas feed mixture containing 50% CO_2, 5% O_2, and 100 ppb SO_2. To maintain long-term electrolyser performance, it was necessary to employ an O_2 removal device to mitigate the negative O_2 effect (Yang & Masel 2021).

Dioxide Materials is working with industrial partners to scale up the electrochemical formic acid technology. Recent research has demonstrated improved performance through improved catalyst design (Díaz-Sainz, et al. 2023; Ozden et al. 2023)

At present, production of formic acid via electrolysis is not as close to commercialization as CO production because of issues with catalyst stability and selectivity. The DNV group found that they needed to reverse the potential to their cell every 2-10 hours to restore catalyst activity. Dioxide Materials regenerates every 7-20 days (Masel et al. 2021).

Very recently, researchers at Massachusetts Institute of Technology reported that the efficiency of electrochemical conversion of CO_2 to formate is strongly influenced local pH and ionic balance across the membranes. They developed a liquid bicarbonate electrolysis system involving a near-neutral-pH cation exchange membrane, a glass fiber intermediate layer, and CO_2 partial pressure management. A test device was operated for over 200 h, converting highly concentrated potassium bicarbonate solution to solid potassium formate with a yield (carbon efficiency) of greater than 96% (Zhang et al. 2023).

9.3.1.2 Victorian Research Context

CSIRO at Clayton currently has a Postdoctoral Fellow working on electrochemical synthesis of formic acid, using a PEM-related approach. Results to date are not promising, with the production of hydrogen more energetically favoured than formic acid.[206]

9.3.1.3 ACI Comments

In Section 7.3.1 it was noted that there are significant thermodynamic barriers to overcome in the catalytic reduction of CO_2 to formic acid. The same situation applies in catalytic reduction of CO_2 by the electrochemical route. International research on this topic is at an early stage, so a pathway toward commercialisation is not yet evident.

ACI does not recommend that this should be a significant research focus in Victoria.

9.4 CARBON NANOFIBRES AND GRAPHENE BY ELECTROLYSIS

Carbon Corp, based in Calgary, Canada is developing a technology platform called C2NT (Carbon Dioxide to Carbon Nanomaterial Technology), invented by Professor Stuart Licht at George Washington University at Washington, DC. In the C2CNT process, CO_2 is bubbled through a bath of

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[206] A. Kulkarni, personal communication

molten lithium carbonate at 770 °C. When voltage is applied across two electrodes immersed in the molten bath, an electrochemical reaction produces O_2 and pure carbon nanonostructures. Research has shown that the product morphology can be altered and controlled by adjusting process parameters, as shown in Figure 108 below.

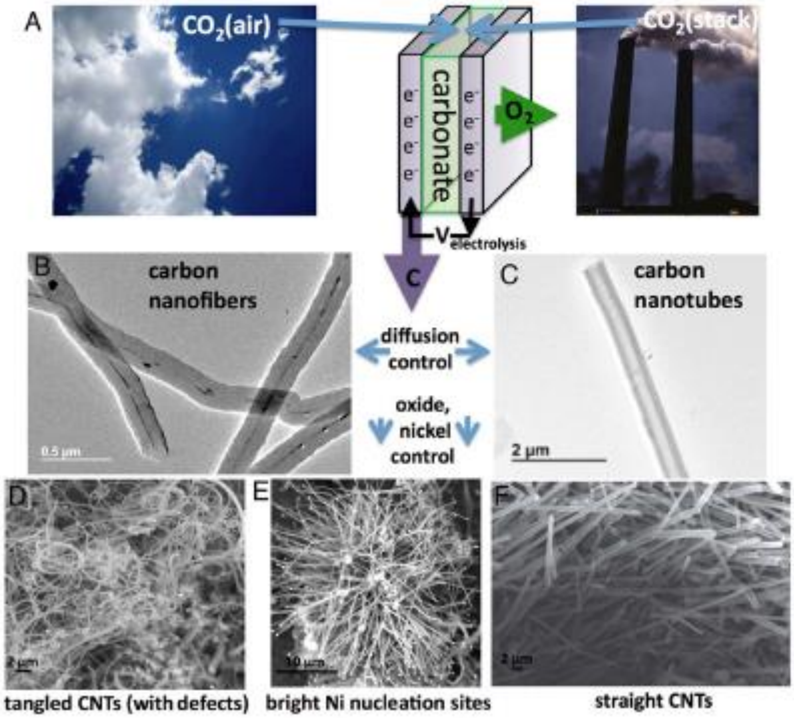

Figure 108: *Electrolytic synthesis of carbon nanostructures from CO_2 (Ren & Licht 2016)*

The main focus of the C2CNT process is to produce carbon nanotubes (CNT) from CO_2, which are flexible, highly conductive and very strong. To date, the principle commercial technology for CNT production had been chemical vapor deposition, which is an order of magnitude more expensive, generally requires metallo-organics rather than CO_2 as reactants, and can be highly energy- and CO_2-emission intensive (Ren & Licht 2016).

The C2CNT process is able to produce CNT wools which can be used in composite materials (Johnson et al. 2017). It can also produce helical carbon nanotubes, nanospiral platelets and graphene (Liu et al. 2020; Liu et al. 2021).

In December 2019, a Canadian power utility company, Capital Power, announced that it would partner incorporate the C2CNT technology in a carbon capture and conversion facility at its Genesee Unit 3. The proposed Genesee Carbon Conversion Centre (GC^3) will demonstrate production of CNTs from CO_2 captured from flue gas. GC^3 will have an initial production capacity of 2,500 tonnes of CNTs per year and once completed will be capable of generating 7,500 tonnes annually. At full scale, the plant is expected to consume 30,000 tonnes of CO_2 per year for use in CNT production (four tonnes of CO_2 are required to produce one tonne of CNTs).[207]

9.4.1.1 Victorian Research Context

There is currently no research under way on this topic in Victoria.

9.4.1.2 ACI Comments

The C2CNT process is subject to a worldwide patent application, so the freedom for others to operate in this area is uncertain.

The level to which the C2CNT process can be scaled up is unknown, given that it involves bubbling CO_2 *through an electrolysis cell containing molten lithium carbonate. Large-scale production of carbon nanotubes by this process seems a long way off, as it is currently at lab pilot scale.*

Given that there are other methods available to produce carbon nanotubes (although not currently from CO_2*), the value-add of the C2CNT process is unclear. ACI recommends a watching brief on this technology to monitor developments.*

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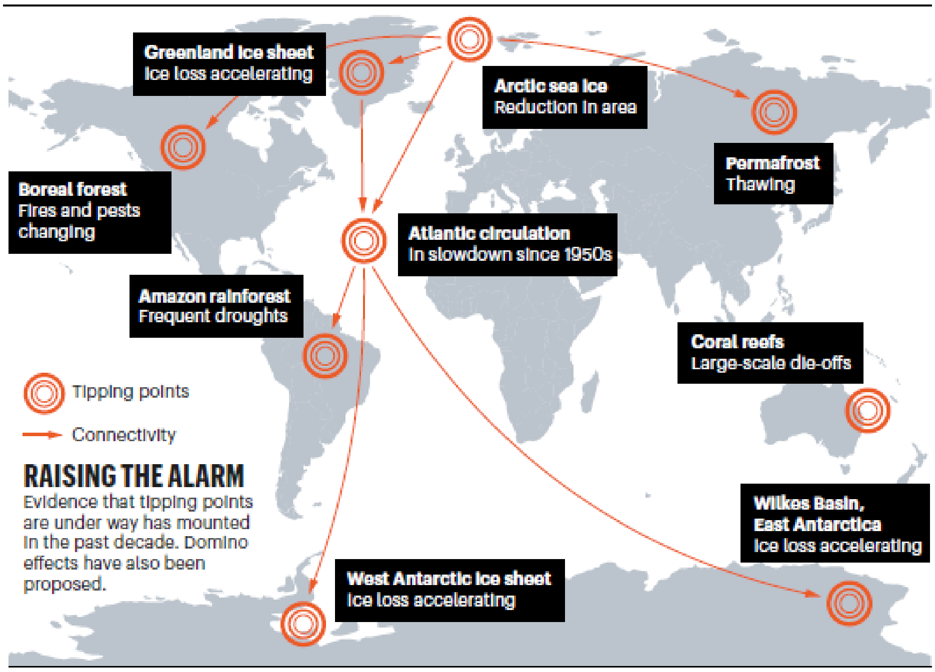
[207] https://carboncorp.org/uploads/GC3_Genesee-Carbon-Conversion-Centre_copy.pdf

10 Appendix 1: Manifesto for a New Green Revolution

"*It is the moral duty of us scientists and our institutions to clearly alert humanity of any potential existential threat and to show leadership in taking action*" (Ripple et al. 2023).

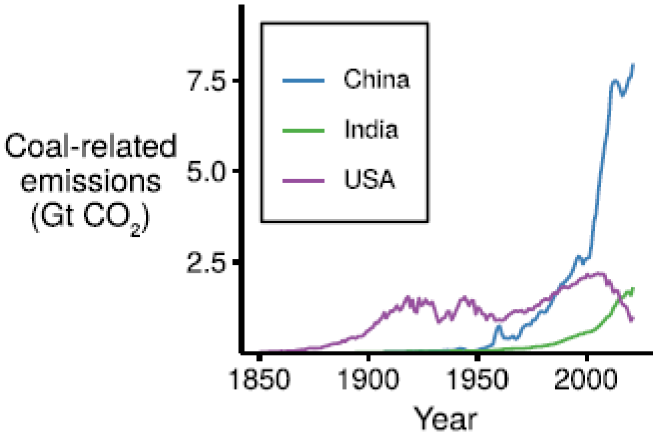
Despite three decades of climate negotiations, carbon dioxide concentrations in the atmosphere have increased from less than 360 parts per million (ppm) in 1992 to more than 420 ppm today– 50 percent higher than pre-industrial concentrations and higher than they have been for millions of years. During that period, average global temperature rose about 0.2˚C per decade to almost 1.2˚C (Harris 2023).

The past eight years have been the warmest on record, and in 2023 an alarming number of climate-related records were broken around the world. Exceptional heat waves have swept across the world, leading to record high temperatures. Global sea surface temperatures have broken records, and there was unprecedented low levels of sea ice surrounding Antarctica. Earth's highest global daily average surface temperature was recorded in early July, possibly the warmest temperature on Earth over the past 100,000 years. The enormous margins by which 2023 conditions have exceeded past extremes is both striking and alarming. The rapid pace of change has surprised scientists and caused concern about the dangers of extreme weather, risky climate feedback loops, and the approach of damaging tipping points sooner than expected (Ripple et al. 2023).



Potential tipping points for catastrophic climate change (Lenton et al. 2019)

After a brief pause in greenhouse gas (GHG) emissions during the COVID-19 pandemic, emissions have continued soaring and fossil fuels remain dominant, with annual coal consumption reaching near record levels. In 2021, coal-related carbon dioxide emissions were greatest in China (53.1%), followed by India (12.0%), and the United States (6.7%). Coal usage in China has accelerated rapidly in the past decades, and the country now still produces nearly a third of all fossil fuel carbon dioxide and methane emissions (Ripple et al. 2023).



Coal-related CO_2 emissions continue to rise (Ripple et al. 2023)

The current pledges under the Paris agreement are insufficient to limit global mean temperature increases relative to pre-industrial levels to well below 2°C. At this stage, 2023 looks set to be the hottest year in 125,000 years,[208] and global warming is expected to exceed 1.5°C in the 2020s and 2°C before 2050 (Hansen et al. 2023).

Warm Boiled Frog © Luojie, China Daily, 2019

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[208] https://www.smh.com.au/environment/weather/australia-weather-2023-hottest-on-record-20231108-p5eij6.html

Temperatures of more than 2 °C above preindustrial values have not been sustained on Earth's surface since before the Pleistocene Epoch, more than 2.6 million years ago. The worst-case scenarios in the IPCC report project temperatures by the 22nd century that last prevailed in the Early Eocene, reversing 50 million years of cooler climates in the space of two centuries (Kemp et al. 2022). Simulation of such temperature rises using a range of Earth System Models suggests the possibility of abrupt changes in sea ice, oceanic flows, land ice, and terrestrial ecosystem response. A particularly large number of abrupt shifts is clustered between 1.5 °C and 2 °C, several of which involve sea ice (Drijfhout et al. 2015).

There is now ample evidence that *Homo sapiens* has become a major force affecting the operation of the Earth system and its biosphere at the planetary level. Reflecting this, a new geological epoch—the Anthropocene, the age of mankind—has been proposed in the Geological Time Scale (Folke et al. 2021). The Anthropocene, which is proposed to have started in the 1950s, is associated with climate change, rapid loss of biodiversity, and rising system-wide turbulence. Distinctive strata reflecting this change have already formed, and many of these planetary changes are effectively irreversible.[209]

Pressure From Heat Waves © Luojie, China Daily, 2022

There are two main reasons for concern over the risk of a global climate catastrophe. Firstly, because climate change (either regional or global) has played a role in the collapse or transformation of numerous previous societies and in each of the five mass extinction events in Earth history. The current carbon pulse is occurring at an unprecedented geological speed and, by the end of the century, may surpass thresholds that triggered previous mass extinctions. Secondly, because climate change could directly trigger other catastrophic risks, such as international conflict, or exacerbate infectious disease spread, and create spillover risk of system-wide synchronous failures that unravel societies across the globe (Kemp et al. 2022).

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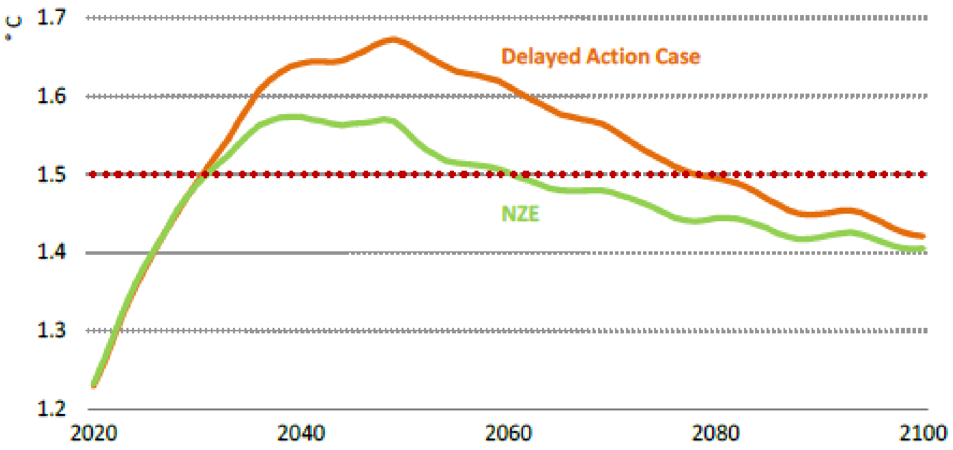
[209] https://www.shh.mpg.de/2347073/anthropocene-working-group-crawford-lake-candidate-anthropocene-site

There is no evidence that the world is, or is on the brink of, making "rapid, far-reaching and unprecedented changes in all aspects of society" that would be required for the deep decarbonization associated with a 1.5°C temperature target (Pielke 2019).[210] To limit global warming to 1.5˚C, global GHG emissions need to fall by almost half within seven years, a period during which they are predicted to rise by ten percent. As the UN Environment Program has noted, currently there is "no credible pathway to 1.5C in place" (Harris 2023). Current GHG emissions put the climate on track of a >3°C warming by 2100 (DeConto et al. 2021).

According to the International Energy Agency, the net zero emissions pledges that have been announced by countries around the world – even if they are all implemented in full and on time – would make it impossible to limit global warming to 1.5 °C without high overshoot (IEA 2023). The net zero emissions (NZE) scenario, which limits global warming to 1.5 °C, can only be achieved with the early closure of existing fossil fuel-based infrastructure and substantial changes to operating patterns.

A more realistic scenario, the Delayed Action Case, assumes that collective efforts will increase and that global GHG emissions will fall by just over one-third by 2035, rather than the nearly two-thirds reduction projected in the NZE Scenario. In this case, the delayed and uneven collective efforts mean that CO_2 emissions reach net zero only by the middle of the 2060s. As a result, the global temperature rise climbs to a peak close to 1.7 °C around 2050. After this time, the temperature falls by about 0.05 °C per decade, bringing warming to below 1.5 °C by 2100. Hence, even a small delay in stronger action to cut emissions beyond current pledges will cause global temperature to exceed 1.5 °C for almost 50 years (IEA 2023).



Median global temperature rise in the Delayed Action Case and the NZE Scenario (IEA 2023)

During Earth's last warm period, 125,000 years ago, melting ice from Antarctica and Greenland caused global seas to rise about 10 metres above the present level. The ice melted first in Antarctica,

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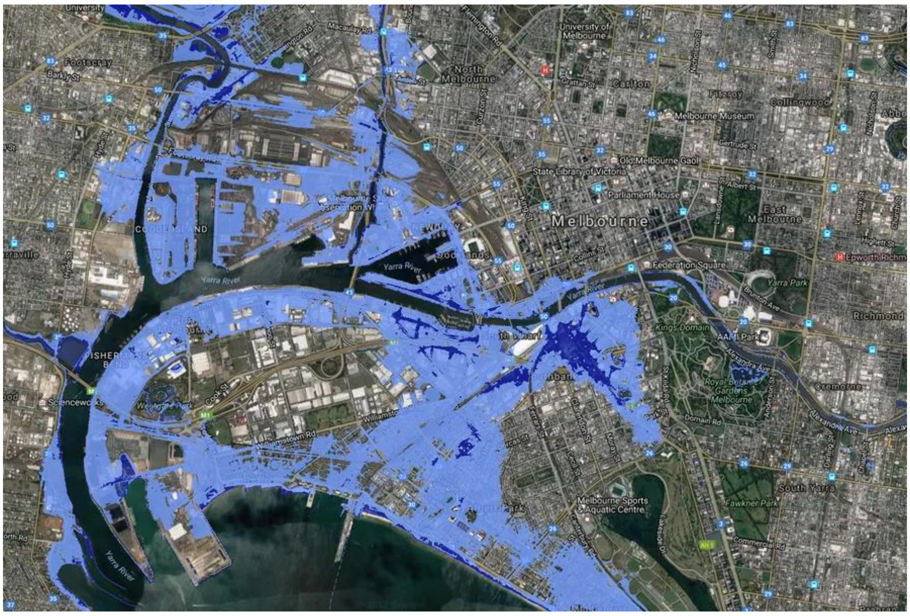
[210] https://www.forbes.com/sites/rogerpielke/2019/10/27/the-world-is-not-going-to-reduce-carbon-dioxide-emissions-by-50-by-2030-now-what/?sh=4e593a883794

then a few thousand years later in Greenland. Sea levels rose at up to 3 metres per century, far exceeding the roughly 0.3-metre rise observed over the past 150 years. Antarctica has been found to be a key player in sea level rise. Its ice sheets can change quickly, in ways that could have huge implications for coastal communities and infrastructure in future (Rohling et al. 2019).

Even the current global temperature rise of 1.2˚C has started to destabilise the Antarctic ice sheet, with rapid thinning and retreat of major outlet glaciers in the West Antarctic being recorded since the early twenty-first century (Sproson et al. 2022). Estimates in the recent literature broadly agree that global mean sea level is likely to rise 20–30 cm by 2050. End-of-century projections diverge more, with typical central estimates ranging from 50–70 cm under representative concentration pathway (RCP) 4.5 and 70–100 cm under RCP 8.5, though more recent projections incorporating Antarctic ice sheet dynamics indicate that sea levels may rise 70–100 cm under RCP 4.5 and 100–180 cm under RCP 8.5, and could even exceed 2m or more in some scenarios (Kulp & Strauss 2019).

In Victoria, the sea level is currently expected to rise by 20, 47 and 82 centimetres at 2040, 2070 and 2100, respectively. More than 16,000 properties in Melbourne’s Southbank are at high risk of damage from sea-level rises and storm surges within 17 years, and Melbourne’s west, Geelong and South Gippsland are also highly vulnerable. It is expected that more than 80,000 currently existing residential, commercial and industrial properties will be impacted by sea-level rise and storm surges by 2100. The cost of property damage is expected to reach $337 billion in present value by 2100, with losses to wetlands reaching a further $105 billion over the same period, bringing the total to $442 billion (Komas et al. 2022).



Large parts of Melbourne are expected to be underwater by 2100 (Coastal Risk Australia)

The Department of Energy, Environment and Climate Action estimates the cost of damage from climate change in Victoria would be over $150 billion by 2050, escalating to about $1 trillion by 2100.

Sea-level rise of 80 cm by 2100 could put at least an estimated $18.3 billion worth of Victoria's coastal infrastructure and assets at risk of inundation and erosion. It estimates that every $1 spent on adapting to climate change now saves society an average of $6 in future costs, and states that Victoria cannot afford to delay action now and pay the price later.[211]

In order to lower the risk of a global climate catastrophe, it is necessary to accept the reality of global warming as an existential threat to humanity, and make every possible effort to reduce the global temperature rise to less than 1.5 °C. It is no longer possible to think that this can be done by shutting down fossil fuel power stations and introducing renewable energy. This should have been done globally at least 10 years ago but the opportunity was squandered. From now on, it will be essential to actively withdraw CO_2 from the atmosphere, in staggeringly large quantities.

Temperature Rising © Pat Byrnes, PoliticalCartoons.com, 2021

The IEA suggests that it will be necessary to scale up CO_2 removal from the atmosphere through bioenergy equipped with CCUS (BECCS) and direct air capture and storage (DACS) to over 5 Gt/y CO_2 during the second-half of this century. By 2100, the Delayed Action Case assumes that CO_2 removal by BECCS will be 2 Gt/y and 3.3 Gt/y by DACS (IEA 2023).

Deployment of BECCS will be restricted by the availability of feedstock or suitable sequestration sites, so DACS will have to do the heavy lifting. However, DACS is much more energy intensive and costly than BECCS, because the low concentration of CO_2 in the atmosphere means that huge volumes of air have to be treated for CO_2 separation. Capturing around 3.3 Gt CO_2 directly from the atmosphere would require filtering 0.1% of the earth's atmosphere every year. At this scale, the IEA estimates that DACS would consume around 3×10^{19} J of energy annually which, if provided by solar PV, would require around 4.5 million ha of land for solar PV and DACS facilities (IEA 2023).

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[211] https://www.climatechange.vic.gov.au/building-victorias-climate-resilience/our-commitment-to-adapt-to-climate-change/adapting-creates-economic-opportunities-and-stronger-communities

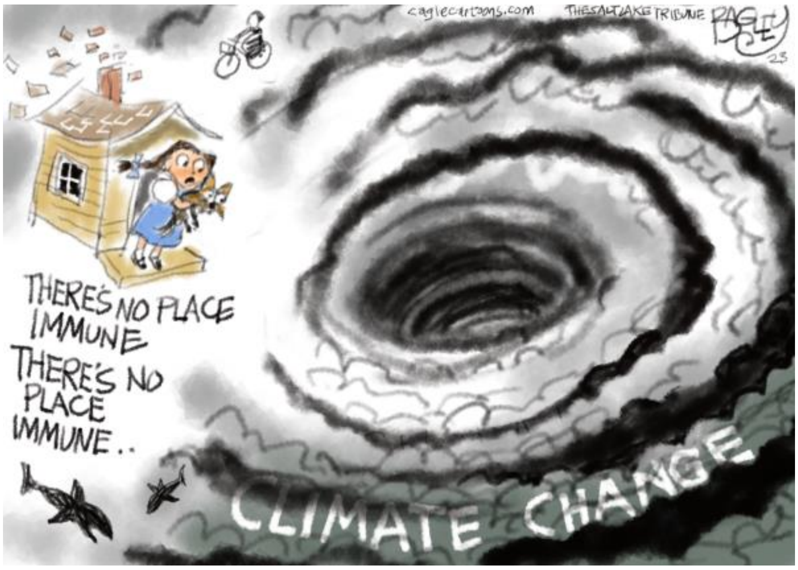
Clearly, this is a daunting challenge, but one that cannot now be avoided. The scale of BECCS and DACS infrastructure that must be installed globally will require a complete transformation of our thinking about energy generation and manufacture. It is no longer appropriate to think in terms of “GHG minimisation” or “net zero emissions”. The focus must now shift to “net negative emissions”, and this must inform decision-making around new power generation and consumer goods manufacture.

Business as usual is placing *Homo sapiens* at risk of extinction. What is now needed is a new Green Revolution in the way our economy is structured. The first Green Revolution completely transformed agricultural productivity through the application of modern crop breeding techniques to the agricultural challenges of the developing world. Scientific understanding of plant genetics led to improved crop varieties that were suited to the growing conditions of the developing world, resulting in yields increasing by 44% between 1965 and 2010 (Gollin et al. 2021).

A new Green Revolution is now needed, not in agriculture but in the way we collectively do business. The existential threat of climate change must be foremost in our decision-making, and new technologies must be developed to make CO_2 capture an integral part of doing business, and products based on captured CO_2 part of our everyday consumer goods. It is only by spreading the load of GHG reduction, to be part of every aspect of society, that the necessary scale of BECCS and DACS infrastructure can be deployed in time.

This means that, as well as improving energy efficiencies and transforming the energy grid to renewables, there needs to be mass cultivation of fast-growing plant species for biofuels and bioproducts, utilise fossil fuels only in combination with CCS, and develop modular, inexpensive systems to capture atmospheric CO_2 for permanent storage. Geological storage of captured CO_2 will not be possible in all locations, so technologies need to be developed to permanently fix captured CO_2 into as many construction materials and recyclable plastics as possible.

Policies to reduce greenhouse gas emissions to net zero must be strengthened to target net negative. The consequences of not doing so will be dire.



We're All Kansas Now © Pat Bagley, The Salt Lake Tribune, 2023

Will *Homo sapiens* live up to its self-appointed title of the "wise ape", or will it squander this opportunity as well? "*This is our moment to make a profound difference for all life on Earth, and we must embrace it with unwavering courage and determination to create a legacy of change that will stand the test of time*" (Ripple et al. 2023).

"*We are alive at the most decisive time in the history of humanity. Together, we can do the seemingly impossible. But it has to be us, and it has to be now*" - Greta Thunberg (Koster et al. 2023).

11 Appendix 2: Definition of Technology Readiness Levels

The technology readiness level (TRL) index was developed by NASA during the 1970s and has since become a globally accepted benchmarking tool for tracking the progress and development of technologies, from blue sky research to actual system demonstration over the full range of expected conditions (Australian Renewable Energy Agency 2014).

The nine different TRLs are defined by CSIRO (Cavanagh et al. 2015) as:

TRL 1: Scientific research begins translation to applied research and development. This is the lowest level of technology readiness. Examples might include basic paper studies of a technology's properties.

TRL 2: Creation and invention begins. Basic principles are observed, practical applications can be invented. Applications are speculative and there may be no proof or detailed analysis to support the assumptions. Examples are limited to analytical studies.

TRL 3: Active research and development is initiated. This includes analytical studies and laboratory studies to validate predictions of separate elements of the technology. Examples include components that are not yet integrated or representative.

TRL 4: Basic technological components are integrated. Fundamental technological components are integrated to establish a system that works well work together.

TRL 5: Reliability of the technology improves significantly. The technological components are integrated with reasonable reliability so it can be tested in a simulated environment. Examples include 'high-fidelity' laboratory integration of the technologies' components.

TRL 6: Model and/or prototype system is tested in relevant or simulated application environment. Model or prototype, which is well beyond that of TRL 5, is tested in a relevant environment. This is a major step-up in a technology's demonstrated readiness. Examples include testing a prototype in a high-fidelity laboratory environment or in simulated operational environment with a publication or technical report documenting the outcomes.

TRL 7: Prototype near or at planned operational system. This represents a major step from TRL 6, in that it requires demonstration of an 'actual' system in an operational 'field' environment.

TRL 8: Technology is proven to work. Technology completed and qualified through commission, testing and demonstration with minor technical issues.

TRL 9: Actual application of technology is in its final form e.g. mature technology. Technology has proven itself through numerous successful operations and can be purchased commercially 'off-the-shelf'.

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