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**Study of amine carbon dioxide capture
and utilisation in the manufacture of
formic acid**

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Declaration

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Abstract

In the light of increasing fears about climate change, greenhouse gas mitigation technologies have assumed growing importance to curb the growing emission from human activities with CO₂ emission having the greatest impact. Carbon capture and storage (CCS) at post combustion point sources has become an attractive route of reducing carbon dioxide emissions into the atmosphere. Absorption by aqueous alkanolamine-solutions is considered the most mature and industrially developed technology for post-combustion capture. Of concern with aqueous alkanolamine-based carbon dioxide capture process is the high energy penalty for the regeneration of the absorbent which has resulting in increased operation costs of carbon sequestration. In order to recover some of the operational cost associated with carbon capture and storage, valorisation technique CCU has been found to offer benefits with hydrogenation products such as formic acid and methanol of particular interest. Pincer based metal complexes have the potential to upgrade amine based carbamates, which are intermediates in the capture of carbon thus present opportunities for integrated capture and valorisation to value added products.

Keywords

Amine absorbents; Carbon capture and utilisation (CCU); Value added materials; Formic acid

Objectives of the study

This study discusses the possibilities of closing the carbon cycle by producing value added products from carbon dioxide captured via the use of amine based solvents. Several critical factors associated with carbon capture and utilisation are clarified under the following sections;-

- the role of carbon dioxide capture and utilisation in lowering greenhouse gas emissions and cost associated with carbon mitigation technology,
- the role of amine based solvent for isolation of carbon dioxide for utilisation to value added products,
- the long-term availability of CO₂ as a prime material for producing value added carbon production such as formic acid or methanol,

Chapter 1

Introduction

CO₂ is a naturally-occurring gas with a major influence in the reflection of solar radiation back to Earth, keeping the planet's surface temperature in levels suitable for the existence of life, (Styring, Quadrelli and Armstrong 2014; Llamas *et al.* 2016). However due to human invention and industrialisation, its concentration in the atmosphere has greatly increased, leading to a rapid rise in the planet's temperature, (Pérez-Fortes and Tzimas 2016). Theoretically, reduction of CO₂ emission in the atmosphere is mainly categorized into three routes, including CO₂ utilization, direct reduction of CO₂ emission, and CO₂ capture and storage (CCS), (Boot-Handford *et al.* 2014; Styring, Quadrelli and Armstrong 2014). With the growing concerns over the increased atmospheric concentration of greenhouse gases, effective CO₂ emissions abatements strategies such as Carbon Capture and Storage are required to curb the trend, (Maginn 2010; Boot-Handford *et al.* 2014; Pérez-Fortes and Tzimas 2016). Data from the Mauna Loa observatory recorded this year (fig 1) have shown that the CO₂ levels have gone beyond the 400ppm threshold, (National Oceanic and Atmospheric Administration 2017), if no measures are taken to limit the increase there is a danger of increasing temperature average going past the 1.5 °C set at the Paris conference, (Llamas *et al.* 2016).

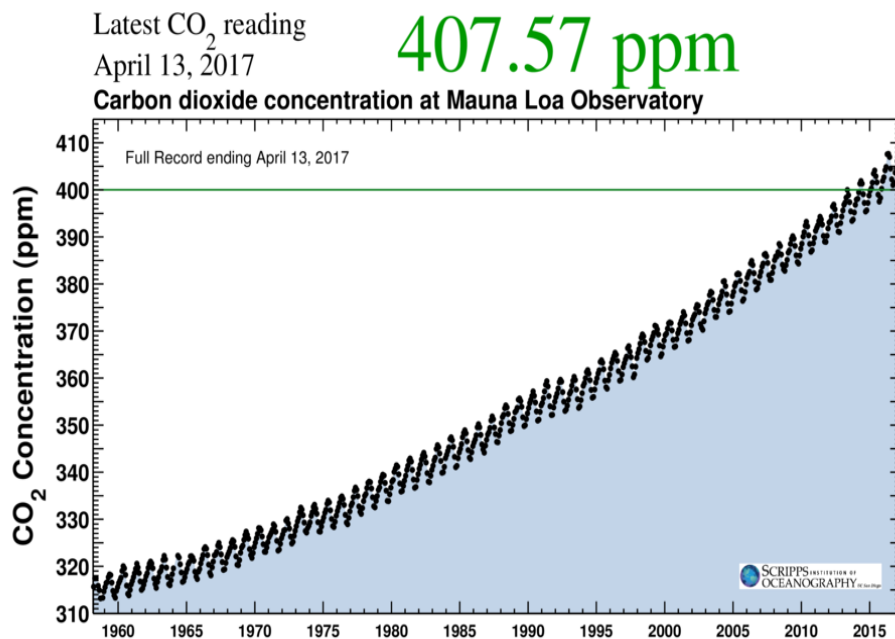


Figure 1, Keeling curve of the atmospheric CO₂, (National Oceanic and Atmospheric Administration 2017)

According to the Global CCS Institute, carbon capture and storage has the potential to significantly reduce the CO₂ emissions to the atmosphere from power plants and chemical industries, such as ammonia, hydrogen, steel and cement production, as well as in fuels preparation and natural gas processing, (Llamas *et al.* 2016). The removal of CO₂ from gas streams can be achieved by a number of separation techniques including absorption into a liquid solvent, adsorption onto a solid, membrane separation and chemical conversion with the methods for capture shown in figure 2, (Boot-Handford *et al.* 2014; Styring, Quadrelli and Armstrong 2014). Today's capture technology is mainly based on chemical absorption with alkanolamines. Even though this is a well-known technology, its application in power plants presents high costs, thus limiting its implementation. Reducing the capture economic penalty associated with carbon capture will allow for wide spread application of the technology and this has prompted the shift towards Carbon Capture and Utilisation, (Boot-Handford *et al.* 2014; Styring, Quadrelli and Armstrong 2014).

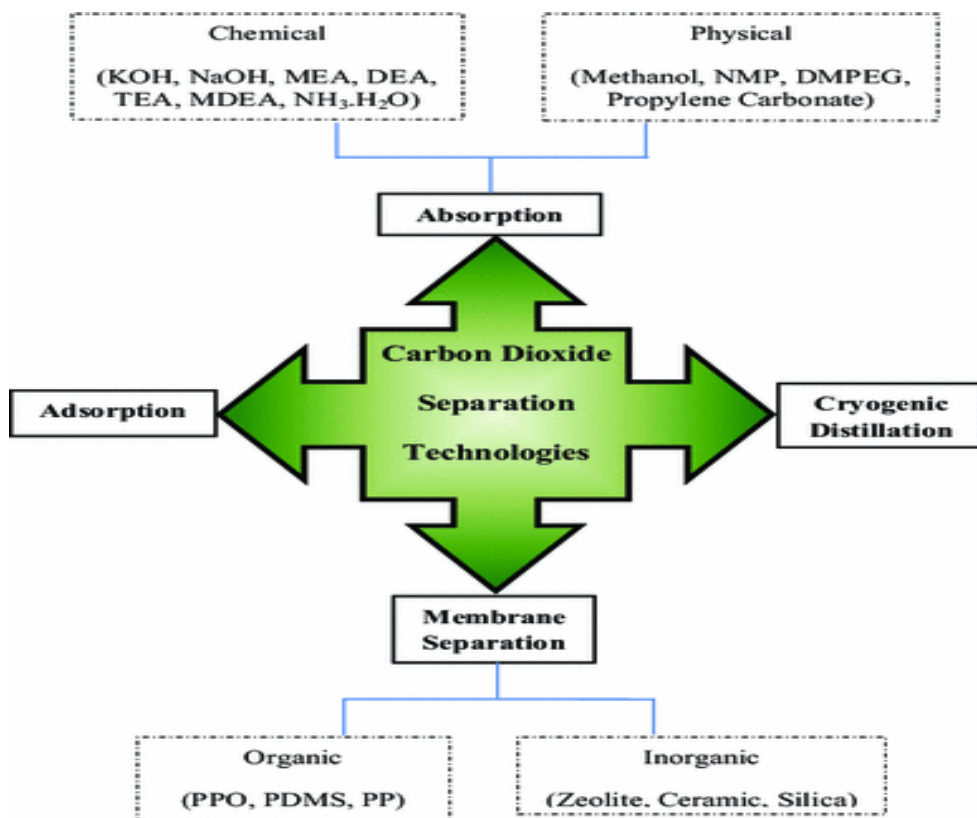


Figure 2, carbon capture techniques, (Llamas *et al.* 2016)

Carbon capture and storage (CCS) is one of the ways in which to deal with the increasing levels of CO₂ from point sources, however significant drawbacks related to possibility of leakage, long-term liability issues, public acceptance and limited cost-effective storage capacity in certain geographic location exist,

(Boot-Handford *et al.* 2014; Llamas *et al.* 2016). The development of end-of-pipe technology (post combustion capture) will allow for the continued utilisation of fossil fuel energy sources while significantly reducing carbon emissions by capturing the carbon dioxide from point source, (Boot-Handford *et al.* 2014; Ganesh 2014). Key enabling technological actors in this context are carbon capture and storage (CCS) and carbon capture and utilization (CCU), since predictions foresee that fossil fuels will retain their central role in energy production worldwide, (Maginn 2010; Llamas *et al.* 2016; Pérez-Fortes and Tzimas 2016). This implies that CCS and CCU (CCUS) will have to acquire the recognition and confidence required to be a viable technology to contribute to any decarbonisation scenario, (Boot-Handford *et al.* 2014). However, extensive energy input in desorption and compression processes have become a barrier to realise practical carbon capture management. Value-added carbon management technologies can generate value-added carbonaceous products such as: fuels, fertilisers, materials and chemicals, (Ganesh 2014). These value-added products may thus offset costs associated with carbon management with some of the applications of utilisation shown in figure 3 below, (Boot-Handford *et al.* 2014; Ganesh 2014). CO₂ utilisation efforts focus on developing beneficial uses of the CO₂ to augment geologic storage as well as offer desirable economic solutions with lower environmental footprint, (Boot-Handford *et al.* 2014).

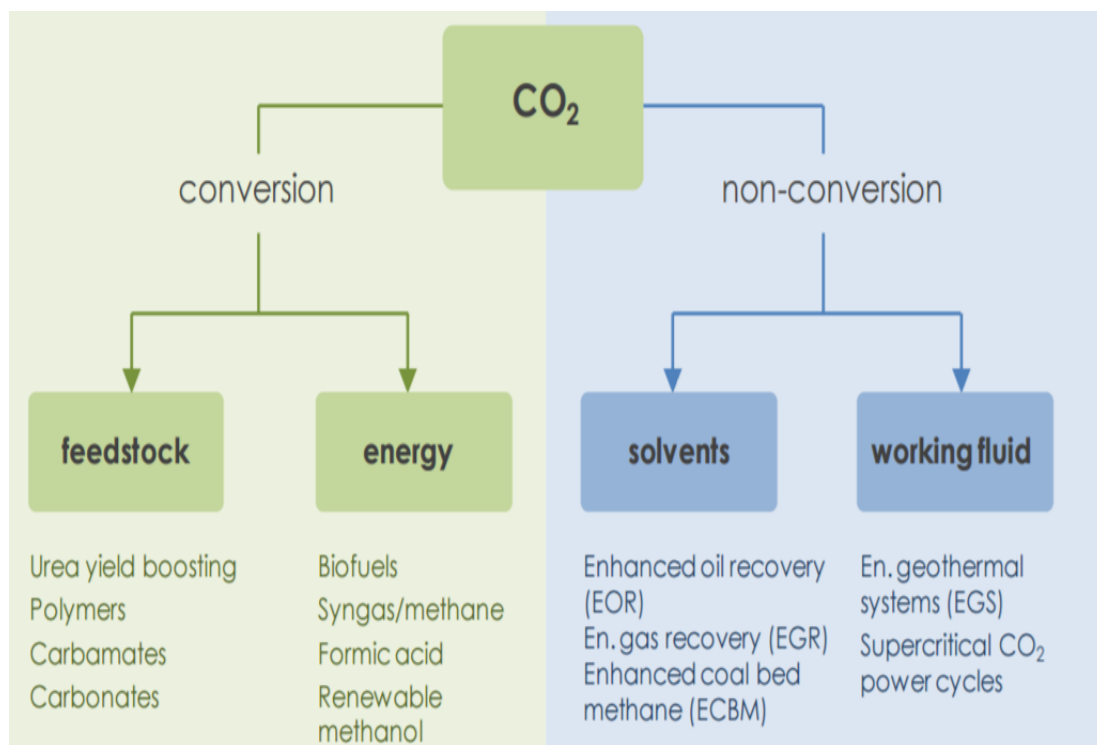


Figure 3, a brief overview of carbon dioxide utilisation routes, (Hendriks *et al.* 2013)

Utilisation of the captured carbon dioxide in parallel with CCS could add value as well as lower the burden on the directly-needed global geological storage locations for the high emissions, (Styring, Quadrelli and Armstrong 2014; Llamas et al. 2016). It holds so much promise from an economic and environmental sustainability point of view as this will reduce the demand for new carbon sources in an era where society is largely dependent on fossil derived carbon sources for fuels and chemicals, (Ganesh 2014; Dimitriou et al. 2015; Llamas et al. 2016). CCU is a valuable complement to geological storage: its potential contribution to avoid CO₂ emissions in the short term has been evaluated at around 300 MtCO₂/yr, used as feedstock in industrial processes and as a working fluid, (Styring, Quadrelli and Armstrong 2014). There is various carbon utilization technologies, which are at different levels of technological and market readiness with urea and methanol the most mature, (Ganesh 2014).

In light of the depletion of fossil fuels and the increased daily requirements for liquid fuels and chemicals, CO₂ should indeed be regarded as a valuable C1 additional feedstock for sustainable manufacturing of liquid fuels and chemicals which is nontoxic, non-flammable, inexpensive, and abundant, (Styring, Quadrelli and Armstrong 2014). While carbon dioxide is considered to be a thermodynamically and chemically stable molecule under standard conditions, it can under certain conditions react with other chemical feedstocks given sufficient energy or using a catalyst to produce value added commodity chemicals, (Boot-Handford et al. 2014). The captured CO₂ will serve as a relatively pure and inexpensive feedstock to synthesize products such as methanol, formic acid, urea, lactones, cyclic carbonates, and polycarbonates, (Styring, Quadrelli and Armstrong 2014).

Traditionally absorption via aqueous alkanolamines has been the most favoured technology for removing CO₂ from process and waste gas stream, (Boot-Handford et al. 2014). Chemical processes based on primary amines such as MEA (monoethanolamine) are preferred when the partial pressure of CO₂ is genuinely very low (less than 1 bar), while chemical processes based on tertiary amines such as MDEA (methyldiethanolamine) are preferred when the partial pressure of CO₂ is slightly higher; MDEA is actually easier to regenerate under these conditions and its lack of reactivity is compensated by the addition of a kinetic absorption activator such as piperazine, (Boot-Handford et al. 2014).

The European Union (EU) has set the objective to reduce greenhouse gas emissions (GHG) by 40% below the 1990 levels by 2030, and down to 80-95% by 2050, (Pérez-Fortes and Tzimas 2016). One of the ways in which the European union and the rest of the global community have agreed on as a means to curtail greenhouse emission is the increased use of renewable

energy in the form of solar and wind, (Maginn 2010; Styring, Quadrelli and Armstrong 2014). Although it is more efficient to use the electrical energy derived from renewable power sources directly, their variability poses a problem for many industries, (Ganesh 2014). It has been difficult for the transportation sector to benefit from this renewable energy form as current engine designs are based on chemical transformation thus suggestion have been put forth to change some of the electrical energy harnessed from the sun and wind to chemical energy in the form of methanol, formic acid (Maginn 2010).

CO₂ can be converted via chemical or electrochemical processes to energy storage chemicals, such as syngas, formic acid, methane, ethylene, methanol, and dimethyl ether (DME), (Ganesh 2014). Catalytic hydrogenation of CO₂ to value added products has been considered as a promising reaction pathway for the utilization of CO₂, (Maginn 2010). This reaction process is not only a remedy for the increasing of CO₂ accumulation in the atmosphere but also a possible solution for energy storage, (Boot-Handford *et al.* 2014). Among products of CO₂ hydrogenation, liquid energy-carriers are an excellent alternative fuel useful as fuel additive, feedstock for fuel cells, and blends with gasoline, (Maginn 2010). Unfortunately, the CO₂ hydrogenation to liquid fuels still has high barriers to overcome including high thermodynamic stability and low reactivity of CO₂ which result in low CO₂ conversion, (Maginn 2010).

Chapter 2

Current status on capture and valorisation of CO₂

The problem of CO₂

The world's carbon dependence has overwhelmed the planet's ability to process the resulting carbon dioxide emissions therefore the challenge on how to restore balance to the carbon cycle exist in today's world, (Styring, Quadrelli and Armstrong 2014; Dimitriou *et al.* 2015). Mitigating global climate change while creating economic opportunities and providing affordable, secure, resilient, and reliable clean energy is one of the preeminent challenges of our time, (Ganesh 2014; Styring, Quadrelli and Armstrong 2014). Global climate change is arguably the most challenging environmental problem facing the 21st century and in order to curb the dramatic growth of greenhouse gases and its related consequences, a broad set of CO₂-limiting policies have been proposed, (Styring, Quadrelli and Armstrong 2014; Yuan, Eden and Gani 2015).

According to the Emission Database for Global Atmospheric Research, global emission of CO₂ current are in excess of 30 billion tonnes, which is 48% more than that of two decades ago. Over the past century, atmospheric CO₂ level has increased more than 39%, from 280 ppm during pre-industrial time to high level of over 400 ppm recorded over the last 3 year resulting in a corresponding increase in global surface temperature of about 0.8 °C which is worrying if society is to keep it below the 1.5°C threshold set at the Paris 2015 summit to avoid irreversible damage to the ecosystem. Mitigation efforts will need to be stepped up to keep up with the increasing emission that is threatening our ecosystem balance.

Proposed solutions

Carbon Capture and Storage (Sequestration) (CCS) has been proposed as a potential method to allow the continued use of fossil-fuelled power stations whilst preventing emissions of CO₂ from reaching the atmosphere. In order to realise true benefits of carbon capture, utilisation techniques that allow for long term or permanent storage have been explored, however there is room to get value added products from the valorisation of CO₂ to fuels and chemicals. Utilisation of CO₂ may involve mostly physical processes, such as in enhanced hydrocarbon recovery (EHR), solvent use, and beverage industry, where the CO₂ is essentially retained in its original state, or chemical transformation, Nevertheless, current global demand for utilisation routes does not have the

capacity to sequester enough CO₂ emission to contribute significantly to the carbon reduction targets.

If recovered CO₂ emissions can be used as feedstock for industrial production processes the existing resource base could be broadened. Especially in the context of circular economy thinking as promoted by the World Economic Forum (2014) making use of waste emissions offers a promising new perspective, (Boot-Handford *et al.* 2014). The development of technically, environmentally, and economically viable ways of utilising CO₂ as a feedstock for industrial production can imply a complementary route to existing mitigation strategies such as the deployment of renewable energy and other green technologies, (Ganesh 2014; Styring, Quadrelli and Armstrong 2014; Dimitriou *et al.* 2015; Yuan, Eden and Gani 2015). Despite headways made in the use of renewable resources as part of carbon dioxide mitigation schemes, certain limitations exist with respect to their storage and intermittent supply, (Boot-Handford *et al.* 2014).

Absorption technique for capture is the most ready technology for industrial scale implementation and it has seen success in the treatment of natural gas and scrubbing of flue gas. The use of alkanolamine in the form of MEA has been spurred on by its low chemical cost, ability to capture CO₂ and fast reaction kinetics. Drawback with regards to solvent regeneration (accounting for more 50% of the overall energy demand), degradation (oxidative/thermal) have limited its usage thus presenting room for improvements.

CO₂ conversion technologies could help meet the ambitious targets set out by the global community to limit GHG emissions by producing valuable hydrocarbons thereby reducing the dependence on fossil resources, (Styring, Quadrelli and Armstrong 2014; Dimitriou *et al.* 2015; Yuan, Eden and Gani 2015). The EU has developed a framework known as the Strategic Energy Technology Plan (SET-Plan) which among other issues encourages the widespread uptake of CO₂ as an alternative carbon resource to produce chemicals, materials, fuels and energy storage means in order to move towards zero carbon emissions. In 2015 the European Commission (COM/2015/6317) held a workshop as part of its broader mandate to discuss how to integrate carbon dioxide utilisation strategy as part of the mitigation strategy making use of high purity source to capture and transform carbon dioxide at minimal cost. High costs and technical issues have led to a wave of high profile project and program cancellations in recent years of carbon sequestration through CCS, the projects cancelled include Norway's Mongstad Carbon Capture cancelled in 2013; four EU utilities pulling out of Zero Emission Platform in 2015 to mention a few. Improving profitability of carbon capture through value added utilisation is more attractive and is in line with current EU commissions' directive of 2015.

The status of Carbon Capture and Storage

Carbon capture and storage (CCS) can potentially store and theoretically fix large volumes of CO₂ in geological media for hundreds of years but without any monetary value (unless enhanced oil recovery (EOR) is done). Cements and minerals made from CO₂ can provide some value, while being able to convert relatively large volumes of CO₂. Carbon Capture and Storage (CCS) consists of three stages; the first being capture of CO₂ from power plants or intensive industries, the second is the transportation of CO₂ via pipeline or ship to a selected storage site, and lastly CO₂ injection into a suitable underground geological formation for the purpose of permanent storage.

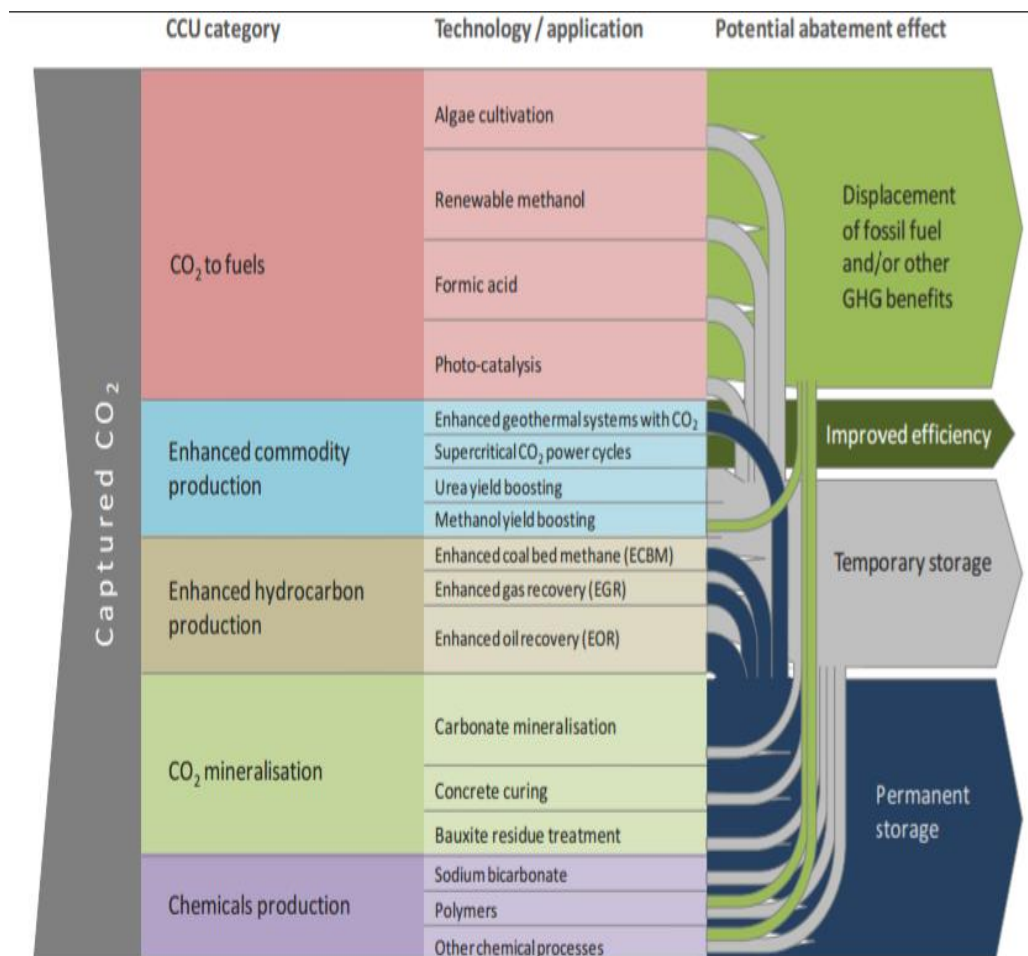


Figure 4, carbon dioxide capture techniques, (Hendriks *et al.* 2013)

Existing CCS projects have already safely captured and stored millions of tonnes of CO₂ and it is a proven effective process. Underground carbon sequestration has been explored as a strategy to curb the increase in atmospheric CO₂ levels, however the energy penalty and high costs associated with the technology has limited its application to date, (Ganesh 2014; Styring, Quadrelli and Armstrong 2014; Wu and Zhou 2016). A key factor that drives

this increase is the energy penalty associated with capture and compression of CO₂ to make it ready for transport and injection. Retrofitting CCS technology to existing stationary point source will allow for decarbonisation of the existing fossil based energy system which society will continue to depend on in the foreseeable future. Non conversion uses resulting in permanent to long term storage carbon have been in the enhanced recovery of hydrocarbons from reservoirs or mineral carbonation. Several utilisation techniques are shown in fig 4 along with their potential lifespan upon implementation.

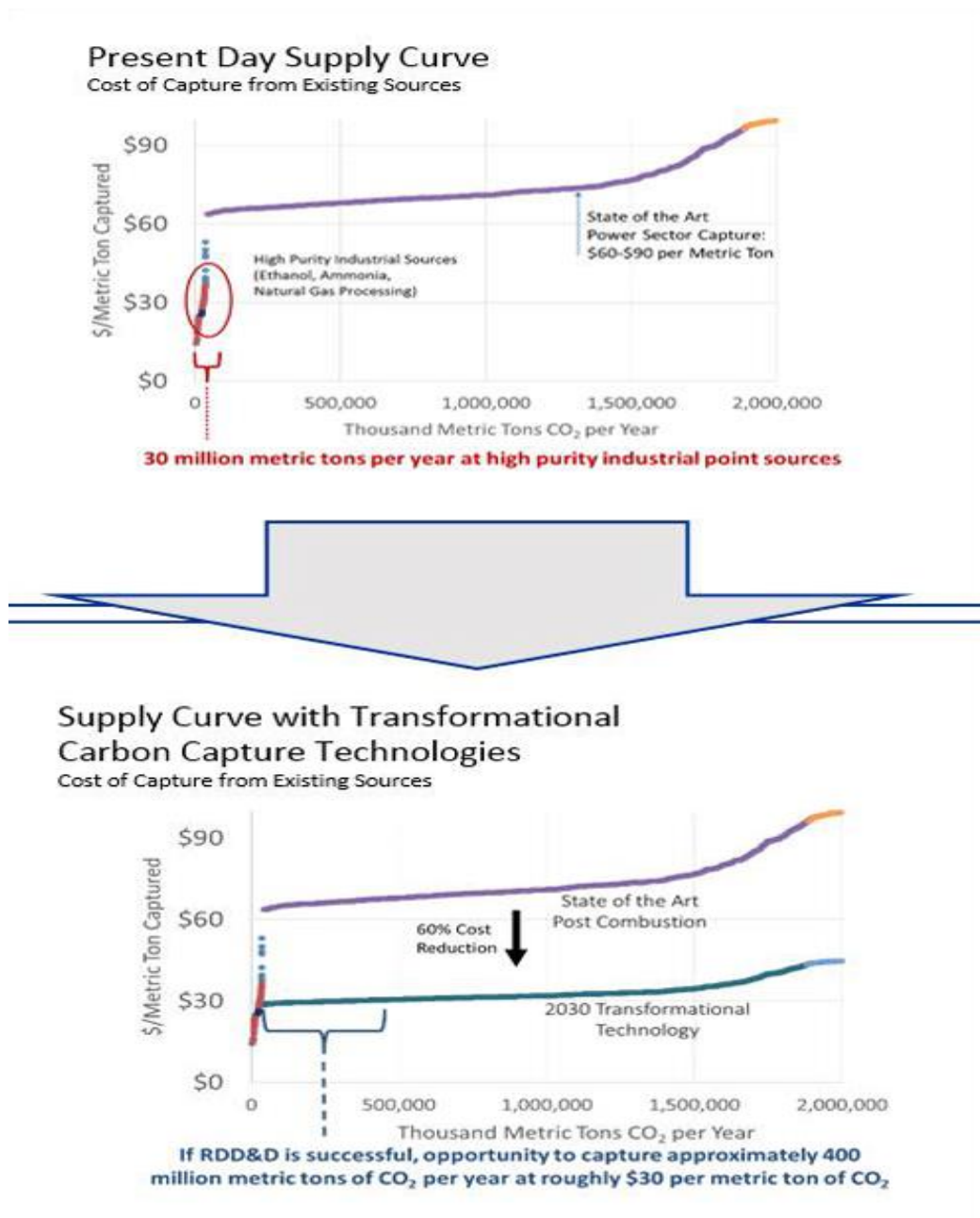


Figure 5, Cost implication of carbon capture technology, (Pérez-Fortes and Tzimas 2016)

Transformative carbon capture shown in the figure 5 highlights the importance of incorporating carbon capture along with utilisation as a means to offset operating cost and generate revenue thus bringing some economic attractiveness to an otherwise costly technology. The scenario shows that a 60% reduction in cost may be expected if part of the capital expenditure is recoupled through the development of value added products with the cost of capture moving to just above \$30 per metric ton of carbon capture from values of \$60 - \$90 per metric ton of carbon capture and stored.

The role of Carbon Capture and Utilisation

The combined system of CO₂ capture with CO₂ re-use is typically referred to as carbon capture and utilisation (CCU) providing raw materials for the production of chemicals, plastics, or fuels and some practical applications as a working fluid. Valorisation of CO₂ appears as a more interesting option than carbon storage, since it allows for the recycling of CO₂ into added-value products as shown in the illustration below. The chemical recycling of CO₂ to produce carbon neutral renewable fuels and materials is considered as a feasible and powerful new approach that is entering the stage of gradual practical implementation, (Ganesh 2014; Styring, Quadrelli and Armstrong 2014; Dimitriou *et al.* 2015). Rather than treating CO₂ as waste, synthesis of fuel and chemical feedstock presents an alternative way to recycle the carbon source thus reduce pressure on conventional sources of carbon, (Styring, Quadrelli and Armstrong 2014; Yuan, Eden and Gani 2015). Production of value added products from CO₂ in theory could offset the cost of carbon dioxide capture making it profitable; however it has been suggested to incorporate the use of renewable energy sources in the facility in order not to throw away the gain made in capture with release of higher emissions, (Styring, Quadrelli and Armstrong 2014). Liquid fuels synthesised from CO₂ can be employed directly in place of fossil fuels without disturbing the present existing energy distribution infrastructure, (Ganesh 2014). The process could be driven by the vast amounts of intermittent excess renewable power that is becoming available in many locations around the world.

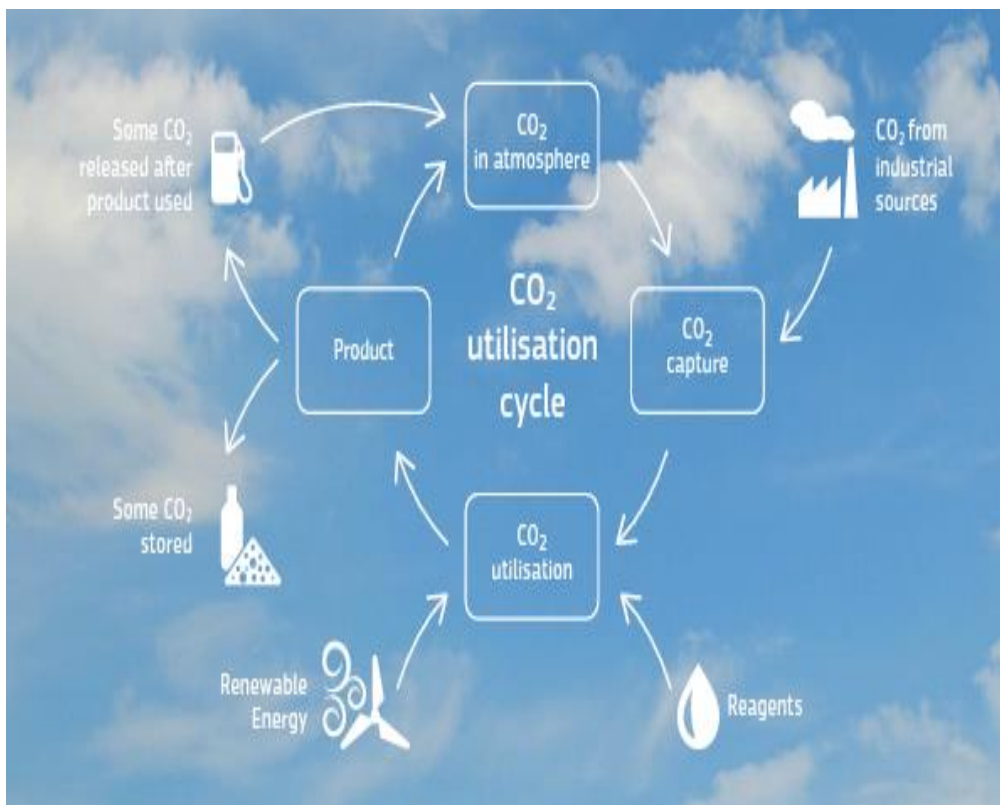


Figure 6, carbon dioxide capture and valorisation, (www.zeroemissionsplatform.eu/ccs-technology/capture 2016)

Even though conversion of CO₂ to various products is energy intensive owing to its thermodynamic stability, the potential for providing a secure supply of chemicals and fuels along with reducing the cost of sequestration has become a powerful driver for carbon capture and utilisation (CCU). Carbon dioxide is one of the most abundant non-fossil carbon resources available, and through technological innovations valorisation of CO₂ could play a vital role in the decarbonisation of industry, (Ganesh 2014; Styring, Quadrelli and Armstrong 2014; Dimitriou *et al.* 2015; Yuan, Eden and Gani 2015). Environmental burden shift should be avoided in the quest to add value to CO₂ and thus most utilisation routes are leaning towards the use of renewable energy supply in order to realise net negative emissions reduction. Negative reviews have also been cast towards the valorisation of carbon to fuel and chemicals with short life span (typically less than six months) as the benefit of capture and utilisation may not practically realised with only a delay of in the release of emissions being realised.

The utilisation of CO₂ to produce synthetic fuels has been explored as part of energy storage routes, harnessing renewable energy sources at off peak times. Introducing CO₂ into the cycle and storing hydrogen by the reduction of CO₂ to hydrocarbons allows renewable energy to be converted into synthetic

fuels with the same energy density as fossil fuels. The resulting cycle is a closed cycle (CO₂ neutral) if CO₂ is extracted from stationary point source. The amount of energy required to produce liquid synthetic fuels has been found to exceed recoverable energy, however its ability to store excess energy in a more usable form is a positive in the quest to add value to carbon emission. Methanol and formic acid have been explored as target products in this regard, upgrading CO₂ via hydrogenation on a wide range of catalyst systems. Methanol synthesis requires three equivalents of hydrogen per molecule of CO₂, two being incorporated into the product with the third being consumed in the production of the by-product, water. Formic acid is a valuable product in that it can store hydrogen in a more manageable liquid form, requiring only a single equivalent of hydrogen and without the formation of by-products and so is highly atom efficient. Formic acid is an organic compound containing 4wt% hydrogen, which is liquid at room temperature and atmospheric pressure. Formic acid is produced by synthesising carbon dioxide and hydrogen with a litre of formic acid storing 600 litres of hydrogen. Subsequent decomposition of formic acid releases the hydrogen when required but also re-releases the CO₂.

Technologies of capture

There are three major process options for CO₂ capture; pre-combustion, post combustion and oxyfuel combustion. Depending on the process, various technologies for CO₂ capture can be employed which include absorption, adsorption, membranes and hybrid applications of the three. At the moment, post combustion capture is the only industrial carbon capture being commercially applied with success. Major example being the Mongstad plant in Norway and the BD3 SaskPower in Canada, however high operational cost are part of the issues that have been slowing down the growth of this industry. The various technologies used in carbon capture are shown in table 1 highlighting some of the advantages and drawbacks associated with each technique.

Table 1 Separation technologies for carbon capture and its application, (Yuan, Eden and Gani 2015)

Technology Option	System Requirements	Advantages	Problems/ Drawbacks
Absorption (Chemical)	Absorber and stripper sections. Chemical sorbent (e.g. MEA, DEA, MDEA)	Suitable even for dilute CO ₂ streams (typical flue gas from power plants). Operates at ordinary temperature and pressure. Commercially available, proven technology	The heat of sorbent regeneration is very high. Significant sorbent losses; pre-processing (e.g. S removal) may be required.
Absorption (Physical)	Absorber and stripper sections Physical sorbent (e.g. Selexol, Purisol and Fluor Processes)	Suitable only for gas streams with high CO ₂ partial pressure (typical syngas from gasification systems). Less energy required, assuming that the gas stream to be processed is already at high pressure. Sorbent are less susceptible to the impurities in the gas stream	Requires high operating pressure. Works preferably with gas streams having high CO ₂ content; so it is not suitable for flue gas processing
Adsorption	Adsorber bed(s)	Commercially available gas separation process.	Low capacity and CO ₂ selectivity of available adsorbents
Membranes	Membrane filter(s)	Upcoming, promising technology with diverse applications. Space efficient.	Requires high operating pressures. Low product purity; need for multiple stages/recycle
Cryogenics	Refrigeration and distillation units	Direct production of liquid CO ₂ .	Requires very large amount of energy for refrigeration (not suitable for dilute streams).

Absorption with amines

Chemical absorption using aqueous amine solutions is one of the oldest technologies (used from 1930) known to treat acidic gases such as CO₂ and H₂S for applications such as natural gas purification and enhanced hydrocarbon recovery, (Barzagli, Mani and Peruzzini 2016). Absorption is currently the preferred option for removing CO₂ from industrial waste gas and for synthesis and natural gas purification, (Kim et al. 2013; Barzagli, Mani and Peruzzini 2016). This process involves passing the flue gas through a liquid that can absorb CO₂ (in an absorber vessel) and then release CO₂ at an elevated temperature in a regenerator vessel (stripper), (Kim et al. 2013).

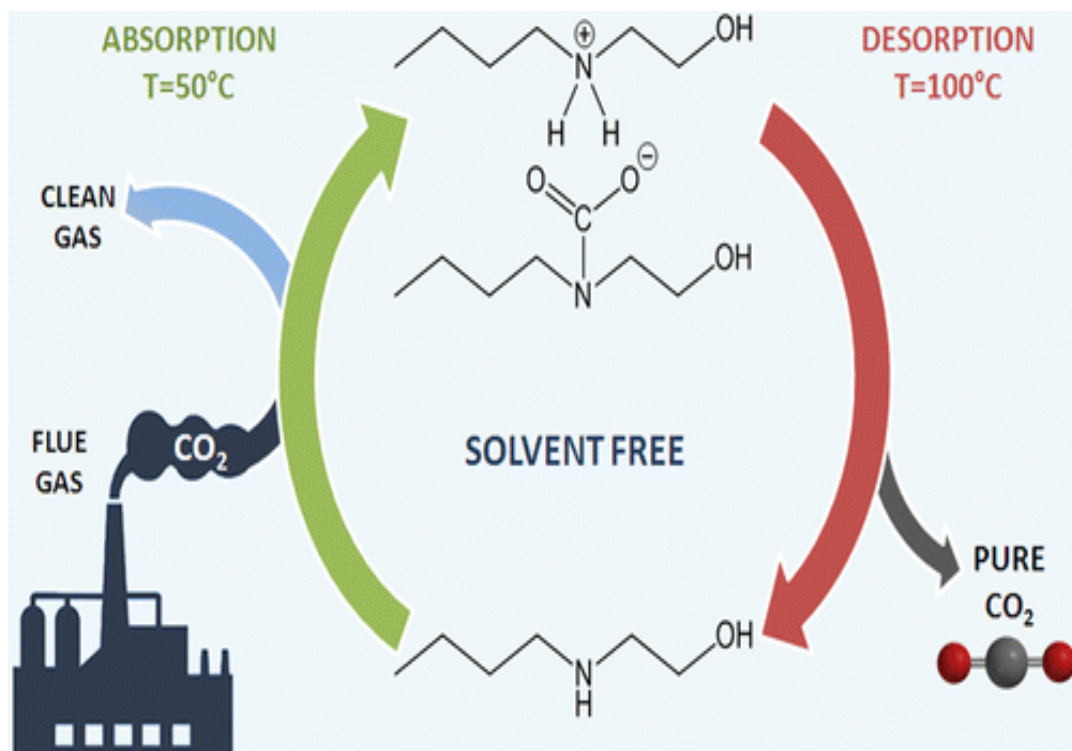


Figure 7, amine based carbon capture from stationary point source, (Barzagli, Mani and Peruzzini 2016)

Post combustion capture, based on mature amine gas separation technology, has seized the largest share of the power market and still offers opportunities for further improvements, (Kim et al. 2013; Barzagli, Mani and Peruzzini 2016). Much of the capture costs stem from handling the huge volumes of low-pressure gases involved in post combustion capture, (Kim et al. 2013; Barzagli, Mani and Peruzzini 2016). However, traditional CO₂ capture process utilising conventional amine solvents is a very energy intensive and is also susceptible to solvent degradation resulting in large operating cost, (Styring, Quadrelli and Armstrong 2014; Yuan, Eden and Gani 2015; Shim et al. 2016).

Typical sorbents include monoethanolamine (MEA), diethanolamine (DEA), piperazine (PZ), methyldiethanolamine (MDEA) and potassium or sodium hydroxide, (Kim *et al.* 2013). The selective and reversible nature with which CO₂ react with amine solution has allowed for capture and recovery of carbon dioxide. In amine based absorption processes, it is estimated that more than half of the capture cost arises from absorbent regeneration, (Kim *et al.* 2013).

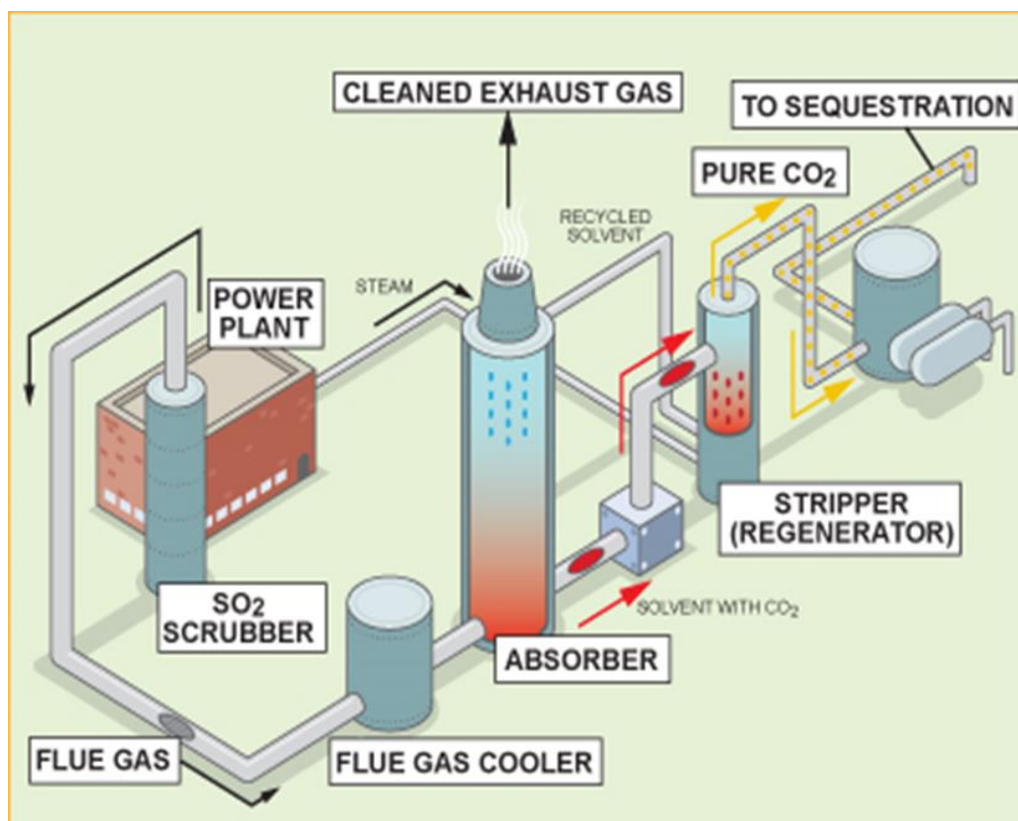


Figure 8 amine based absorption for carbon dioxide capture, (Dash and Bandyopadhyay 2013)

The primary and secondary alkanolamines react faster with carbon dioxide with the formation of carbamate species, (Amann and Bouallou 2009; Kim *et al.* 2013; El Hadri *et al.* 2017). Heat of absorption for the reaction with primary and secondary amine is very high which corresponds to increased regeneration energy of the solvent, (Amann and Bouallou 2009; El Hadri *et al.* 2017). The maximum theoretical CO₂ loading of the primary and secondary amines is 0.5 mole of CO₂/mole of amine (two molecules of amines is needed to react with one molecule of CO₂), (Kim *et al.* 2013; El Hadri *et al.* 2017). The CO₂ loading of the tertiary alkanolamines is higher with a maximum of 1 mole of CO₂ per mole of amine; one molecule of amine react with one molecule of CO₂ and this reaction does not form carbamate but it forms bicarbonates, (Amann and Bouallou 2009; El Hadri *et al.* 2017). The tertiary alkanolamines reactivity with CO₂ is lower in comparison with the primary or secondary

amines, (Amann and Bouallou 2009; Kim *et al.* 2013; El Hadri *et al.* 2017). Thus, the heat of absorption associated with this reaction is lower and the energy required to regenerate the amine solvent will be reduced, (Amann and Bouallou 2009; El Hadri *et al.* 2017).

Table 2, Heat of absorption of CO₂ in aqueous amine solution (30wt%, 313.15 K and atm. Pressure), (El Hadri *et al.* 2017)

Type of sorbent	Heat of absorption kJ/mole CO ₂	Loading capacity (moles of CO ₂ per moles of absorbent)
Monoethanolamine (MEA)	- 85.13	0.59
Diethanolamine (DEA)	-74.24	0.61
N-Methyldiethanolamine (MDEA)	-52.51	0.74
2-amino-1-methyl-2- propanol (AMP)	-80.91	0.78
Piperazine (PZ)	-80.58	0.91
3-dimethyl-amino-1- propanol (3DMA1P)	-54.55	0.85
2-(dimethylamino) ethanol (2DMAE)	-63.26	0.77

The low heat of absorption for MDEA is because of the formation of unstable carbamates, and this results in low activity in the capture process despite the high loading capacity associated with tertiary amine, (Amann and Bouallou 2009; El Hadri *et al.* 2017). Piperazine and 2-amino-1-methyl-2-propanol (AMP) show reasonably high heat of absorption which means in aqueous solutions of capture they form relatively more stable carbamates but the bulkiness of these amines has been known to result in higher loading capacity capture as weak bicarbonates intermediates are formed increasing the capture capacity, (El Hadri *et al.* 2017). The presence of carbamates influences the regeneration efficiency of alkanolamines solutions, as these stable compounds are difficult to revert to fresh amine, leading to longer regeneration times and greater energy consumption. In contrast, sterically hindered alkanolamines, like AMP form unstable carbamates due to the hindrance of the bulky group, (Artanto *et al.* 2014). Comparing the regeneration performance of different well-known conventional alkanolamines gives the following order: AMP > MDEA (N-methyl diethanolamine) > DETA (diethylenetriamine) > DEA (diethanolamine) > MEA. Another advantage of

AMP solutions is their higher CO₂ loading capacity (1 mol of CO₂/mol of AMP, versus 0.5 mol of CO₂/mol of MEA), (El Hadri et al. 2017). Piperazine (PZ) has been studied as an activator increasing carbon capture capacity with its ability to form weak carbamates with one mole of amine capturing an equal molar of carbon dioxide where for primary amine half a mole is captured on the same basis, (Artanto et al. 2014). Interest has recently grown in mixing alkanolamines to reduce energy loss and solvent degradation, (Artanto et al. 2014). To achieve cost effective carbon capture the choice of solvent used in absorption is critical, with research done to date showing that stationary carbon sources releasing effluent at low partial pressure are not suited to the use of MEA, (Dash and Bandyopadhyay 2013; Artanto et al. 2014). Piperazine with a cyclic, diamine structure has been found to facilitate rapid formation of carbamates with a theoretical capacity to absorb two moles of CO₂ for every mole of amine thus it has found increasing use as a promoter to the various amines available, (Artanto et al. 2014; El Hadri et al. 2017).

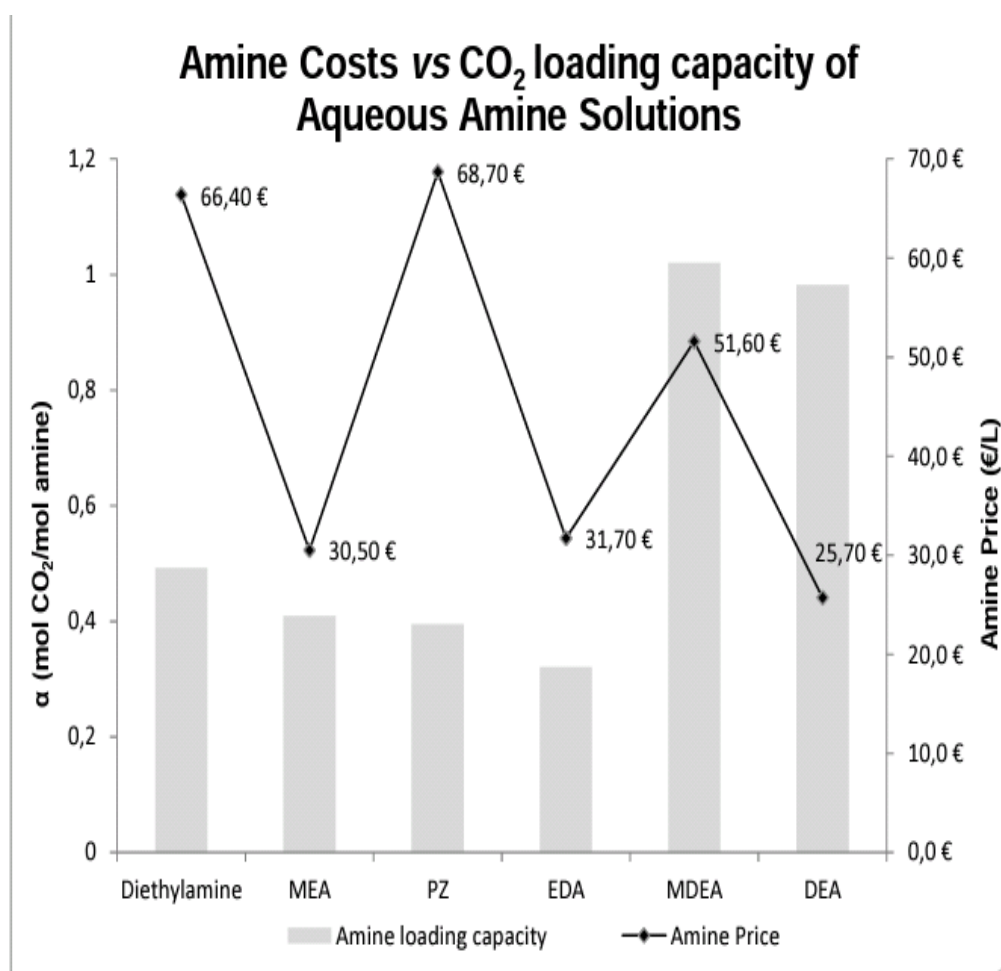


Figure 9, Amine cost vs loading capacity of aqueous sorbent solutions, (Gomes, Santos and Bordado 2015)

The state-of-the-art process making use of 15–30 wt% aqueous monoethanolamine (MEA) has been plagued by many challenges such thermal and oxidative degradation, corrosiveness, high vapour pressure leading to high loss of sorbent leading to high make up stream as well as high energy penalty for regeneration, (Dash and Bandyopadhyay 2013; Artanto *et al.* 2014). Studies have shown that tertiary amines such as the cyclic piperazine (PZ) and 2-amino-2-methyl-1-propanol (AMP) are easier to regenerate with less loss of absorption capacity than other amines, such as MEA, diethanolamine (DEA), diethylenetriamine (DETA) and N-methyldiethanolamine (MDEA), (Dash and Bandyopadhyay 2013; Artanto *et al.* 2014) and this has led to increased research into their utilisation. Critical factors to look at in choosing sorbents for capture should include low or moderate corrosiveness, high degradation resistance and relatively lower regeneration energy requirement, (Dash and Bandyopadhyay 2013; Artanto *et al.* 2014). Solvent emissions and degradation products can be environmentally harmful, and dealing with them can increase operating costs.

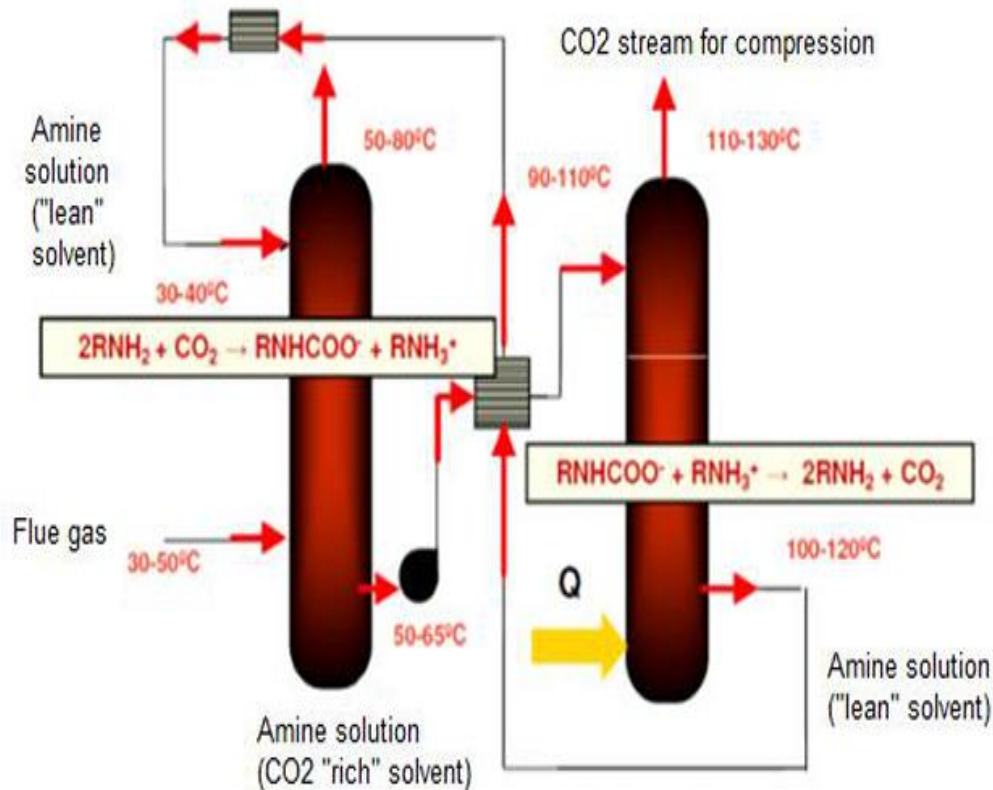
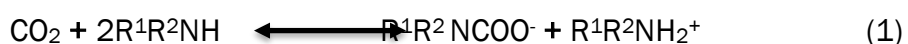


Figure 10, Amine based capture process diagram with reactions and temperature conditions, (Gomes, Santos and Bordado 2015)

CO₂ reacts with amines in the absorber according to reactions 1 and 2





The process captures CO₂ primarily via carbamate formation as expressed in reaction 1 or via bicarbonate formation as per reaction 2. The reversible nature of the amine capture allows for the release of the captured carbon dioxide when energy supply is increased in the stripper section. Higher temperatures in the absorber section favour the breakdown of the amine and this has been responsible for loss of capture capacity and amines, (Boot-Handford *et al.* 2014). The high energy penalty related to amines regeneration (a high-intensive energy process because of the stripper operating conditions and solvent used) and solvent degradation are the issues most hindering a large deployment of this technology, (Boot-Handford *et al.* 2014). Oxidative degradation of amine solvent is a major source of solvent loss in carbon dioxide capture with some studies qualitatively identifying the products as organic acids, ammonia, and amides. Amine degradation must be minimised to manage secondary environmental impact and corrosion of equipment. Thermal degradation is reported to account for 20-30% of total amine losses; hence the maximum operating temperature of the amine re-boiler and stripper system is determined by thermal degradation, (Boot-Handford *et al.* 2014). By using amine solvents at CO₂ capture facilities, it can lead to the release of amines emissions to the atmosphere and pose risk to human health and natural environment.

Ammonia has been explored as an alternative for CO₂ capture with lower energy consumption and the possibility of recovering fertilizer as the main arguments to promote its application in a large scale, (Boot-Handford *et al.* 2014). Aqueous or chilled ammonia has better loading capacity, no corrosion problems, stable in flue gases conditions, lower liquid to gas flow ratio, less energy consumption during the regeneration of solvent (if the ammonia is recovered instead of used to produce NH₄HCO₃, (NH₄)₂SO₄, and/or NH₄NO₃), and it is more economic than MEA. Chilled ammonia process uses aqueous ammonium salts (such as ammonium carbonate) to capture CO₂ that can make use of waste heat to regenerate the CO₂ at elevated temperature and pressures to reduce downstream compression, (Boot-Handford *et al.* 2014). This process will generate less problem as compared to those that amine is facing with degradation. The chilled ammonia process allows for higher stripping temperature which results in the release of CO₂ at higher pressure than is possible with the amine solvents making for ease of integration of conversion process, (Boot-Handford *et al.* 2014). Research is on-going to improve the cost and energy demands of CO₂ capture and utilisation compared to conventional technologies and this has seen the development of non-aqueous solvent systems or ionic solvent systems.

Conversion technologies

As mentioned earlier the main challenge of utilising CO₂ as a chemical feedstock is its unfavourable thermodynamics. Interestingly amongst the various valorisation techniques, the need for hydrogen is common, (Agarwal *et al.* 2014). this has presented an opportunity to solve hydrogen storage problems with carbon dioxide valorisation to synthetic hydrogen storage compounds such as formic acid, formate with higher energy density storage capacity per unit volume, (Agarwal *et al.* 2014). Electrochemical, photochemical and thermochemical transformations have been explored in this regards resulting in the formation of synthetic hydrogen storage compounds. Over the years various works have been done on heterogeneous hydrogenation of CO₂ to synthetic hydrogen storage, however operating conditions have been characteristically high (>200 °C) affecting the entropically unfavourable reduction reactions, (Agarwal *et al.* 2014; Rezayee, Huff and Sanford 2015). Homogenous catalysts have been explored to overcome the challenges of heterogeneous catalyst in thermochemical upgrading of CO₂ (Agarwal *et al.* 2014; Rezayee, Huff and Sanford 2015).

Electrochemical reduction of CO₂

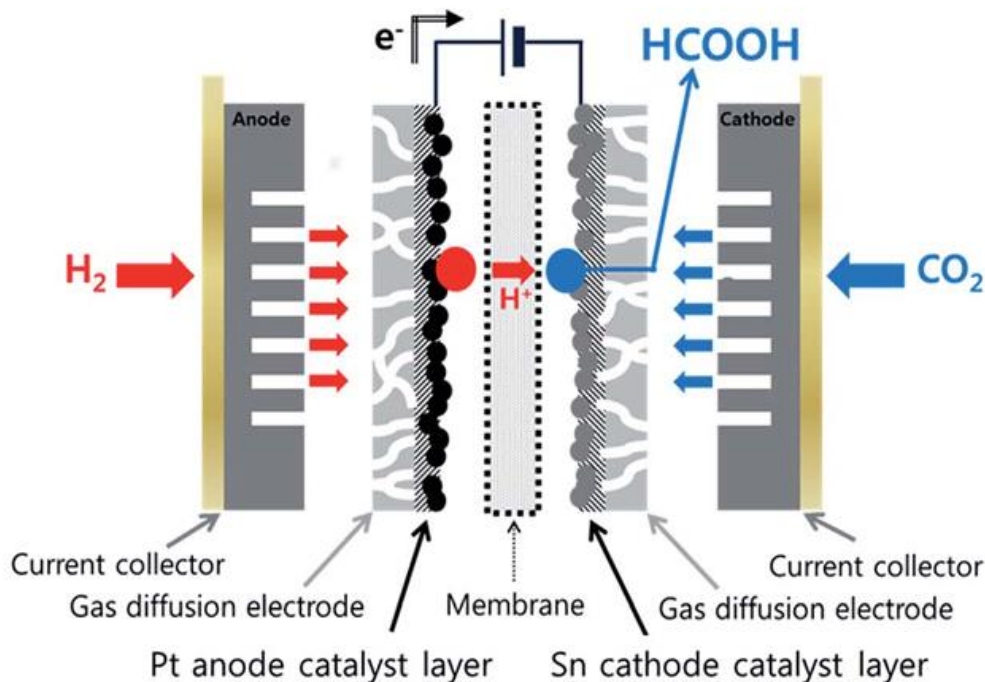
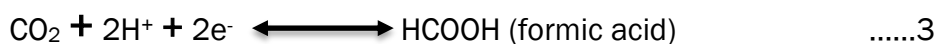


Figure 11, electrochemical reduction of CO₂ to formic acid, (Lee *et al.* 2015)



Electrochemical reduction of CO₂ into value added chemicals appears to be better than traditional thermochemical processes operating at mild reaction conditions, (Agarwal *et al.* 2014; Lee *et al.* 2015). High selectivity of formic acid from electrochemical reduction of CO₂ is found on metals with high hydrogen overpotential such as indium (In), lead (Pb), mercury (Hg), and tin (Sn) (selectivity ranges from 65% to 100% depending on the metals, CO₂ pressure, and electrolytes, (Agarwal *et al.* 2014; Lee *et al.* 2015). This process could be the most convenient way of storing electrical energy in the form of liquid fuels without increasing additional CO₂ emissions. Tin shown in the illustration above (Fig 11) may be the most practical candidate for production of formic acid as it has been studied extensively in the literature, as well as its availability, cost, and low toxicity to humans, (Agarwal *et al.* 2014). By employing suitable electrode and catalytic systems, very high Faradaic efficiency could be achieved in electrochemical process. A reaction with high Faradaic efficiency means a lower energy requirement to complete the reaction, (Lee *et al.* 2015).

Synthetic chemical hydrogen storage

Part of the strategy to curb CO₂ emission proposed include the use of fuel cell electric vehicles which presents a great opportunity to utilise formic acid as it has a higher capacity to store and release hydrogen which will burn cleanly emitting water with carbon dioxide recycled, (Agarwal *et al.* 2014; Moret, Dyson and Laurency 2014; Lee *et al.* 2015). Formic acid is considered as one of the most promising materials for hydrogen storage today, (Yoo 2013). H₂ is a potential clean energy source, but as a result of problems associated with its storage and transport as a gas, chemical H₂ storage (CHS), which involves the dehydrogenation of small molecules, is an attractive alternative, (Agarwal *et al.* 2014). Currently established hydrogen storage technologies include compressing hydrogen at high pressures (350 or 700 bar), liquefying hydrogen at low temperatures (below 20.3 K), or storing hydrogen as chemical/metal hydrides, (Agarwal *et al.* 2014). These technologies, however, suffer from high costs, low energy densities, loss of hydrogen, and safety issues, (Yoo 2013).

In principle, formic acid (FA, 4.4 wt % H₂) and methanol (MeOH, 12.6 wt % H₂) can be obtained renewably and are excellent prospective liquid chemical H₂ storage materials, (Yoo 2013; Moret, Dyson and Laurency 2014; Lee *et al.* 2015). In addition, MeOH has considerable potential both as a direct replacement for gasoline and as a fuel cell input. The current commercial syntheses of FA and MeOH, however, use nonrenewable feedstocks and will not facilitate the use of these molecules for CHS, (Moret, Dyson and Laurency 2014; Lee *et al.* 2015).

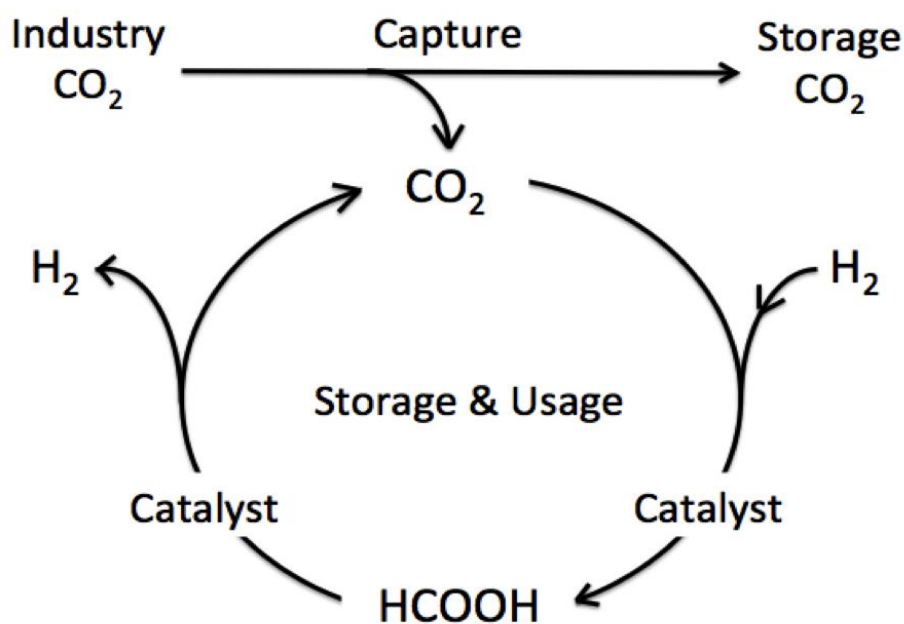


Figure 12, schematic showing carbon dioxide valorisation to formic acid, (Yoo 2013)

Formic acid potential as an energy carrier

Formic acid is a well-known chemical that has potential as hydrogen carrier and as fuel for fuel cells, (Pérez-Fortes and Tzimas 2016). Formic acid finds its applications in textiles, pharmaceuticals and food chemicals, due to its strong acidic nature and reducing properties, (Pérez-Fortes and Tzimas 2016). Formic acid is a high valued product, with a concentrated, small and mature market, with low risk of substitution. A number of studies describe the potential of FA for H₂ storage, as a non-toxic and easy-to-store chemical, i.e. as a liquid through integrating renewable energy capture (biomass, solar or wind to power electrolysis) to reduce the environmental footprint, (Pérez-Fortes and Tzimas 2016). Formic acid can be directly used in fuel cells.

Given its non-toxicity and high energy density (far exceeding that of most other H₂ storage materials used today), formic acid is an ideal H₂ storage material with enormous potential to meet the power needs of small fuel cells for portable applications, (Yoo 2013; Moret, Dyson and Laurency 2014; Lee *et al.* 2015). This is largely driven by the fact that H₂ gas currently derived from non-renewable natural gas or petroleum is highly explosive, thus, posing significant safety concerns and the need for alternative safer and more effective technologies, (Moret, Dyson and Laurency 2014; Lee *et al.* 2015).

An appealing option for the sustainable synthesis of both FA and MeOH, which could be implemented on a large scale, is the direct metal catalyzed hydrogenation of CO₂. Furthermore, given that CO₂ is a readily available,

nontoxic and inexpensive source of carbon, it is expected that there will be economic and environmental benefits from using CO₂ as a feedstock, (Moret, Dyson and Laurency 2014). Figure 11 below shows potential net negative emission reduction realised through the adoption of utilisation techniques such as hydrogenation to synthetic liquid fuels. Formic acid production through the utilisation techniques mentioned will realise a greater emissions reduction potential as more carbon is sequestered per ton of product.

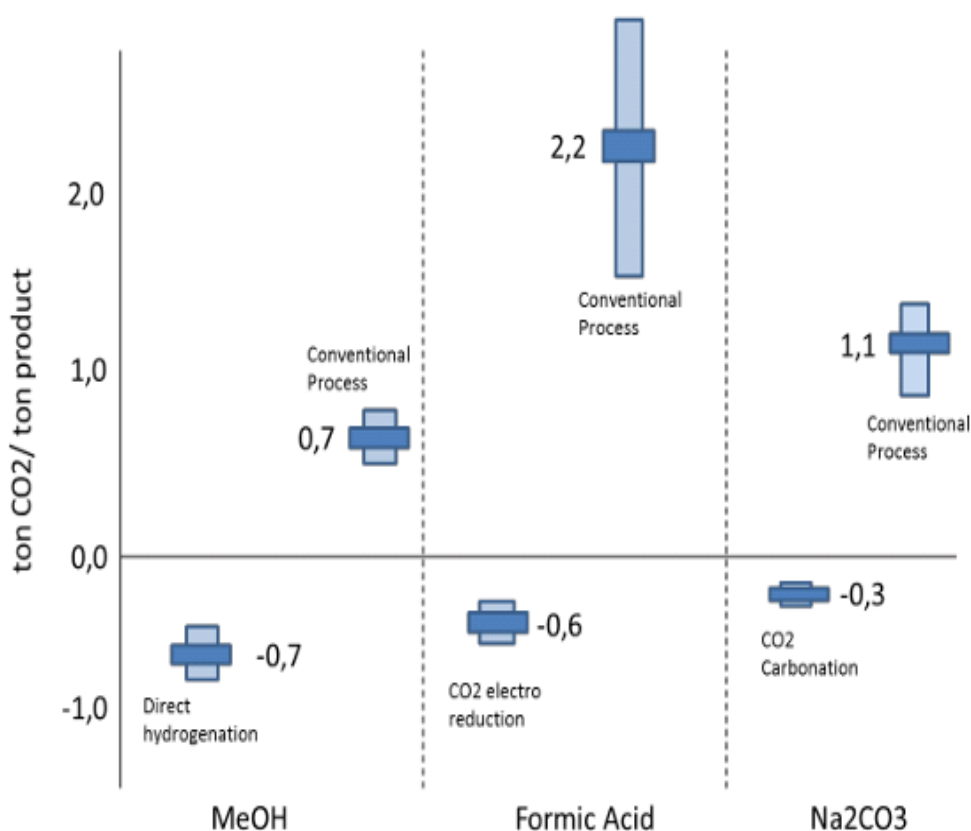


Figure 13, CO₂ emission reduction potential utilisation routes, (Dimitriou *et al.* 2015)

Hydrothermal based reduction

Many iron, cobalt, ruthenium, iridium, and rhodium based homogenous catalysts have been explored for the hydrogenation of carbon dioxide to formate salts which can function as synthetic hydrogen storage, (Rezayee, Huff and Sanford 2015). Homogeneous transition metal catalysts such as zinc selenide/zinc telluride have been used for direct hydrogenation of carbon dioxide, (Moret, Dyson and Laurency 2014). Ruthenium complexes have also gained attention as homogenous catalyst in the presence of nitrogen-containing bases resulting in the formation of reduced hydrocarbons as shown in the fig below where methanol is formed via the proposed reaction

mechanisms,(Rezayee, Huff and Sanford 2015). Recently progress has been made in the hydrogenation of amine based carbamates intermediates in the capture process in homogeneous based aqueous solution catalyst in the form of metal complexes such as the one shown below in fig 14 based on the ruthenium material.

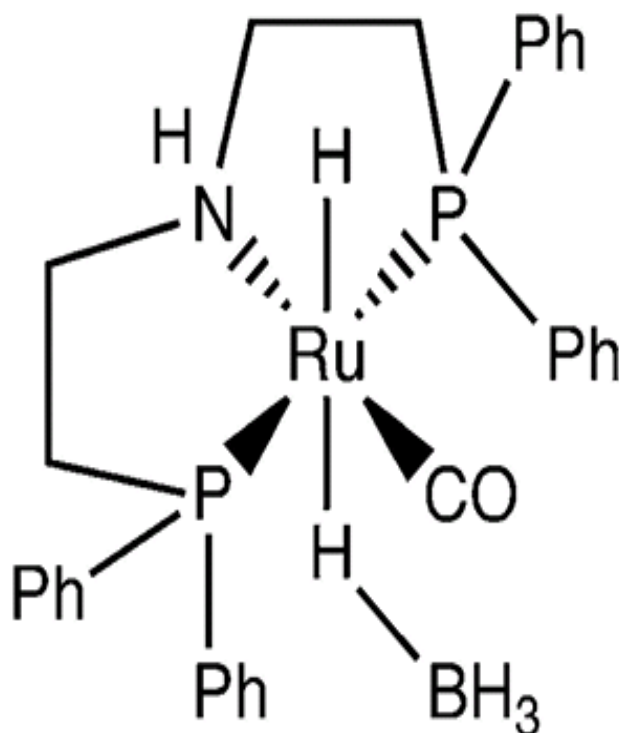


Figure 14, metal based complex for the hydrogenation of amine based carbamates, (Agarwal et al. 2014)

The class of catalysts complex shown in fig 14 above is known as pincer catalyst systems and they have the potential to hydrogenate amine based carbamates in homogeneous phase. This may prove advantageous in integrating amine based capture with valorisation to fuel and chemicals as they have proved useful in the formation of synthetic hydrogen storage liquids such as formic acid and methanol. In the work done by Rezayee, Huff and Sanford (2015), methanol was formed over the ruthenium complex catalysts and the proposed reaction mechanism is shown in fig 15 below. Potential benefits of such an integrated processing of capture and valorisation include reduced cost as the costly amine regeneration and carbon dioxide compression steps are avoided, (Rezayee, Huff and Sanford 2015). More work need to be done however with different metal complex in homogeneous phase to see the potential for commercial application.

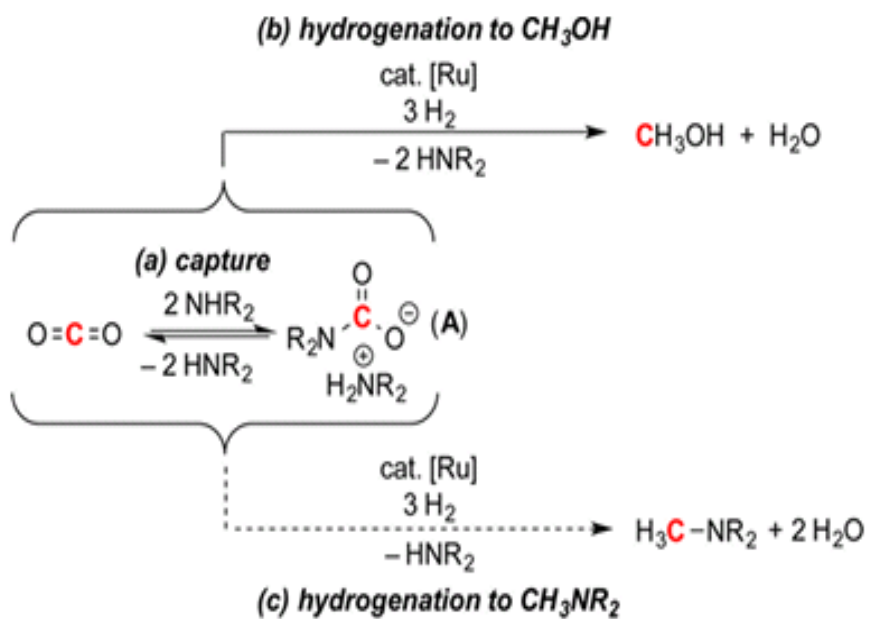


Figure 15, ruthenium based amine hydrogenation of CO₂, (Rezayee, Huff and Sanford 2015)

Conclusion

Increasing carbon dioxide levels could be controlled by CCU technology, producing useful and voluminous carbon based fuels and chemicals to reduce the environmental footprint of combustion. Integrating amine based carbon capture and valorisation will allow for the realisation of carbon mitigation schemes in an economical viable manner. Conclusions that can be derived from the survey are that the cost of amine has a significant influence on the commercial application with the study by showing that DEA has the highest potential in terms of cost and carbon loading capacity. However the most widely used commercial amine MEA pricing is not too far away despite having a lower loading capacity. Piperazine which is being utilised as an activator to increase loading of unhindered amine seems to be fairly priced which may increase its practical application if availability in voluminous quantities is sorted. Lower heat of absorption and high loading capacity factors shown in table 2 can be used to determine the best applicable amine for carbon capture and from the data provided MDEA is ideally placed to be the best suitable candidate. However low kinetics and high sorbent cost have seen its application limited and current research has been exploring the use of activators such as piperazine to improve the kinetics of capture thus allows for increased loading capacity in mixed amine blends with materials such as MDEA and DEA which have low kinetic. Recycling of carbon via utilisation techniques such as hydrogenation to synthetic liquid fuel is best placed to allow for easy storage of excess renewable energy through chemical hydrogen storage. There is a need for more work to be done to realise the integration of the amine capture and carbon valorisation. Metal complexes such as the ruthenium pincer have the potential to be integrated into amine based capture to produce value added products such as methanol and formic acid, however there is room for more practical work to be done with such complexes before commercial applications. It is my strong recommendation that experimental work be done with homogeneous metal catalyst complexes that fall in this group of pincer catalysts to gain more insight and data.

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