A Call to (Green) Arms: A Rallying Cry for Green Chemistry and Engineering for CO2 Capture, Utilisation and Storage.

Journal:	*Green Chemistry*
Manuscript ID	GC-PER-06-2018-001962.R1
Article Type:	Perspective
Date Submitted by the Author:	15-Aug-2018
Complete List of Authors:	Leclaire, Julien; Université Claude Bernard Lyon 1 - CNRS, UMR 5246 ICBMS - CSAp Heldebrant, David; Pacific Northwest National Lab, Applied Synthetic Chemistry

Journal Name

PERSPECTIVE

A Call to (Green) Arms: A Rallying Cry for Green Chemistry and Engineering for CO_2 Capture, Utilisation and Storage.

Received 00th January 20xx,
Accepted 00th January 20xx
DOI: 10.1039/x0xx00000x
www.rsc.org/

Julien Leclaire and David J. Heldebrant

Abstract

Chemists, engineers, scientists, lend us your ears… Carbon capture, utilisation, and storage (CCUS) is among the largest challenges on the horizon and we need your help. In this perspective, we focus on identifying the critical research needs to make CCUS a reality, with an emphasis on how the principles of green chemistry (GC) and green engineering can be used to help address this challenge. We identify areas where GC principles can readily improve the energy or atom efficiency of processes or reduce the environmental impact. Conversely, we also identify dilemmas where the research needs may be at odds with GC principles, and present potential paths forward to minimise the environmental impacts of chemicals and processes needed for CCUS. We also walk a different path from conventional perspectives in that we postulate and introduce potential innovative research directions and concepts (some not yet experimentally validated) in order to foster innovation, or at least stoke conversation and question why certain approaches have not yet been attempted. With elements of historical context, technological innovation, critical thinking, and some humour, we issue a call to arms and hope you may join us in this fight.

Introduction

Anastas and Warner wrote in their seminal work that, “Green chemistry involves the design and redesign of chemical syntheses and chemical products to prevent pollution and thereby solve environmental problems.” Twelve principles of green chemical engineering came later on to complement the 12 principles of GC and constitute a full set of guidelines for technical approaches to make processes more environmentally benign.[1, 2]

Green chemistry (GC) launched under the auspices of making chemical processes more environmentally benign. The majority of early GC research focused on identifying less-toxic reagents, on reducing the non-renewable inflows and impacting outflows in order to minimise the global environmental imprint. GC has many success stories, helping humanity move the chemical industries away from toxic and carcinogenic reagents such as phosgene ($COCl_2$), remove volatile organic compounds (VOCs) and lead from paint, develop biodegradable plastics and detergents through catalytic processes (such as metathesis), significantly reduce the waste production and water consumption, respectively, associated with drug manufacturing and textile processing. GC also led to the development of many catalytic processes that increase yields and rates of chemical processes with reduced emissions and waste streams.

GC should not be pigeonholed as an environmental movement; GC is also an economic driver. GC has been shown to enhance the economics of chemical processes by using sustainable, renewable energy and resources, sourcing cheaper and more cost-effective reagents, with increased atom economy and energy efficiency. Further, less-toxic and biodegradable reagents and waste streams reduce costs associated with waste disposal, minimize adverse effects from exposure to harmful chemicals and avoid bioaccumulation. This is evident as chemical companies would only adopt new processes in the absence of regulation if there were a monetary incentive to do so. Thus, we champion the premise that any of the 12 principles go beyond making chemical processes more environmentally benign; they also make processes cheaper and more streamlined.

The 12+12 principles of GC and green engineering (GE) have been used successfully for decades to tackle many individual chemical processes, though these wins are pale in comparison with the magnitude of the next challenge on the horizon, climate change. Among the many potential fields of application where GC should change the world, the most obvious and challenging is sustainable development. Sustainable development encompasses GC and GE because it involves, beyond the environmentally benign manufacturing practices, the societal goal to improve human and environmental well-being. This notion of well-being is associated with a straightforward and widespread access to a spectrum of commodities ranging from breathable air, drinkable water, and affordable energy to manufactured goods. Apart from the first one, which still is free, the remaining ones involve a cost in energy for their production and delivery. Reducing this energy demand, which reaches up to 15% of global consumption, is undoubtedly a challenge for green chemists and engineers.[3] Regarding the end products from human activities, this ever-increasing global energy demand is continually driving the upward trajectory of global CO_2 emissions. The annual volume of global anthropogenic CO_2 emissions was 36.8 gigatons in 2017; to put things in perspective, that amount of CO_2 by our calculations would equal the volume of Crater Lake in Oregon (18 km^3) and next year's emissions will surpass the volume of Lake Geneva (20 km^3). The Intergovernmental Panel on Climate Change drafted a report that quantified a global "carbon budget" (Fig. 1),[4] which is the amount of CO_2 emissions that can be emitted with a high degree of probability of limiting global temperature rise to the IPCC and COP21 warming target of ~2° Celsius above pre-industrial levels.[5,6] As of early 2018, humans have emitted over 70% of the Earth's 2,900,000,000,000-ton proposed carbon budget, suggesting we may exceed the projected global 2 °C increase target as agreed upon in the Paris Climate Accord.[6] Thus, there is an urgent need to deploy technologies that reduce emissions to minimise the greenhouse effect and potential effects of climate change.

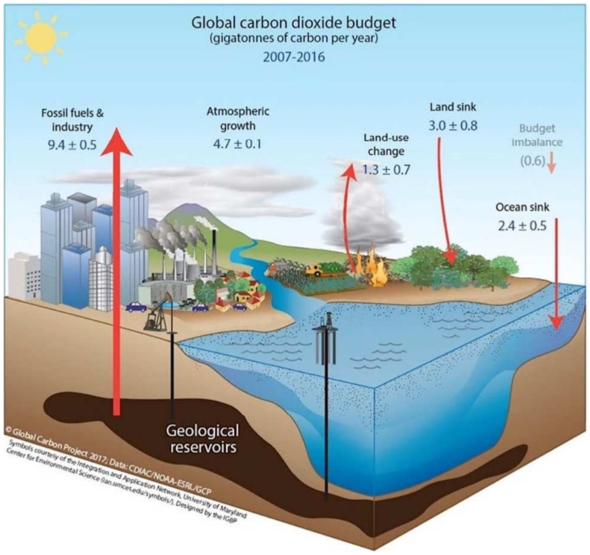

Fig. 1. CO_2 budget. CDIAC; NOAA-ESRL; Le Quéré *et al.* 2017; Global Carbon Budget 2017[4]

CCUS (carbon capture, utilisation and storage) is an encompassing acronym that represents a collection of chemical sciences and technologies covering the entire life cycle of CO_2. We point to a definitive review of current CCUS technologies that has recently been reported.[7] There is more to CCUS than just capturing CO_2 from anthropogenic sources; it also includes compression of CO_2 for transportation, either to permanent geological storage or reconstitution into value-added products. CCUS also includes the industries who manufacture the infrastructure, and chemical industries who supply and synthesise materials for capture, waste handling and disposal, environmental health and safety, and long-term monitoring. Each of these aspects is energy and cost intensive. The principles of GC can be used to improve efficiency and lower costs while also making the processes more environmentally benign. These processes should not be considered individual problems; they are a single chain of value, from cradle to grave, which relies on an integrated network of multiple disciplines and industries and requires a synergistic effort to make CCUS successful.

Humankind's carbon-based fuel cycle has created a colossal looming challenge, at a scale that borders on the unfathomable. The removal of gigatons of CO_2 will require *gigajoules of energy* to power technologies using *gigatons* of sorbent, which will require *gigatons of solvent* to be synthesised, which begets *gigatons of waste*. Any realistic approach to CCUS will have to do less environmental harm than good. Thus, the paradox is, how can CCUS be green, when the chemicals, infrastructure, and energy required for CCUS are so vast? The best way to answer the paradox is to first identify the components of the problem.

We envision CCUS as a five-headed "hydra" like the creature of Greek mythology, with each head being a challenge or opportunity for GC and GE to address (Fig. 2). We identify its heads as: (1) The operational expenditures (OPEX), which are the energy inefficiency of capture technologies; (2) The capital expenditures (CAPEX), which include the materials and process infrastructure; (3) The life cycle of the capture infrastructure, spanning synthesis, use, and waste; (4) transportation and storage of CO_2; and (5) utilisation, which includes reconstitution and storage into value-added products. Each of these heads has historically been addressed individually, but unified green approaches are necessary to make CCUS feasible.

Fig. 2. Conceptual CCUS five-headed Hydra.

Throughout human history, tales have spoken of valiant heroes who rise to battle the forces of oppression and ride off into the sunset. With CCUS, there is no Heracles sent from the gods to lead us in battle, there are no or vorpal blades can go “snicker-snack” and slay this Jabberwock that humanity has created. Current efforts in CCUS are attempting to slay each head individually through compartmentalised and isolated efforts. As with the beast in Greek mythology, cutting off one of the CCUS’s heads individually is likely to make it grow two more. As often in the chemical sciences, replacing a toxic or harmful substance with a new greener alternative may result in unintended and unforeseen consequences down the road. With CCUS, we must be sure that technologies that are developed to mitigate greenhouse gas emissions do not introduce new unforeseen hazards.

Herein we issue a call to (green) arms, we call upon our colleagues from all scientific disciplines to take up arms and combine their forces and expertise to join the fracas. Idleness has allowed this problem to grow each year, making it progressively harder to subdue. The time for action is now. To slay such a beast requires binding all of the heads of the hydra together in a concerted and synergistic assault using the principles of green chemistry as our sword and green engineering as our shield.

Discussion

In this perspective, we focus on tackling CCUS with a technological focus on solvent-based CO_2 capture from post-combustion sources, though these concepts and insights can readily be adapted for pre-combustion or other gas streams. The primary reason for solvent-based technology is that it is the only commercially deployed technology, albeit for natural gas. There are many promising membrane[8] and porous materials[9] technologies in development and we believe they may benefit from the different disruptive approaches or “out of the box” suggestions we selected herein. We also limit discussion on CO_2 capture from industrial gas streams because they are the lowest hanging fruit from a cost and concentration standpoint. Direct air capture has seen recent advances to \$150/tonne CO_2,[10] but thermodynamically and financially speaking, removing gigatons of CO_2 from air (400 ppm) is still more costly than removing CO_2 from flue gas (150,000 ppm).[7] If some of the disruptive approaches described herein may lead to viable and sustainable CCUS value chains from CO_2-rich flue gases, they may serve as solid foundations to further design CCUS systems operating directly from air. Under these auspices, we look at each of the five heads of the hydra as areas of need, where we identify challenges for which the principles of GC could provide the innovation and concepts to enhance solvent-based CO_2 capture. We also emphasise that the concepts explored here aim to attack more than one head at a time.

1. Head #1. Process inefficiency

The first head of the CCUS hydra is the energy costs required for the separation of CO_2 from mixed gas streams—the OPEX.

The primary limitation for solvent-based CO_2 capture is the parasitic load on the coal-fired power plant. Bolting-on a solvent-based capture technology introduces a 20% parasitic load to the power plant; *i.e.,* an average sized 500 MW plant will lose 100 MW of power to the CO_2 capture unit.[11] Coal-fired power plants then burn *more* coal to bring the plant back up to nameplate capacity, thus releasing more CO_2 into the atmosphere and creating a vicious cycle.

To get a perception of the magnitude of carbon capture processes, consider how big the problem really is. A medium-sized 550 MW coal-fired power plant will emit 3 M kg/h of gas, of which 454,000 M kg/h is CO_2.[11] The world’s largest coal-fired power plant, the Taichung Power Plant in Taiwan is ten times larger than an average plant at 5,500 MW, emitting over ~40 M tonnes of CO_2 annually through smokestacks that are over 250 m (890 feet) tall (Fig. 3).[12] The challenge of CCUS is designing a process that can be bolted onto the exhaust stack of a power plant that can capture a molecule that is thermodynamically and kinetically relatively stable (CO_2) under dilute concentrations (10–15 vol%) at millions of kg’s per hour of gas flow in the presence of highly reactive impurities such as nitrogen oxides (NO_x) and mixed oxides of sulphur (SO_x). Assuming the United States’ optimistic target of 90% CO_2 capture, a solvent-based process would require solvent circulation rates on the order of millions of kg per hour per power plant and process infrastructure that is commensurate in size.[11] Granted, the 90% capture target is quite ambitious, and lower levels of capture have been considered, but we encourage the higher target as it will help negate the effects of climate change. In either case, post-combustion CO_2 capture is a daunting task.

Fig. 3. Taichung Power Plant, Longjing**,** Taichung**,** Taiwan, 5,500 MW coal-fired power plant. Emissions ~40 M tonnes per annum. Stacks are 250 m high.

Solvent-based CO_2 capture is not new, having been first patented in the 1930s by Bottoms to remove CO_2 from natural gas.[13] Aqueous solutions of CO_2-reactive amines have been the backbone of solvent-based processes for over 80 years. In the many decades since, the chemistry has remained mostly the same, though there have been advancements in engineering and configurations that have resulted in efficiency gains. Today, there are multiple commercial offerings from notable companies such as Fluor, Shell, Mitsubishi Heavy Industries, and BASF, though the lowest reported reboiler duty has been reported for CANSOLV at 2.3 GJ per tonne of CO_2.[14] The sizeable energy penalty is primarily due to the energy-intensive step of regenerating the solvent, which involves pumping, boiling, and condensing millions of litres of water per hour and, to a lesser extent, compressing of captured CO_2 for subsequent transportation (Fig. 4).[15] *Strategy for Head #1: GC must focus on reducing the energy required to perform the separation.*

Aside from known phenomena and exploitation of physical properties of organic solvents that have been covered elsewhere, here are some unique concepts, processes, or physical or thermodynamic phenomena that we feel GC could and should consider for potential efficiency gains.

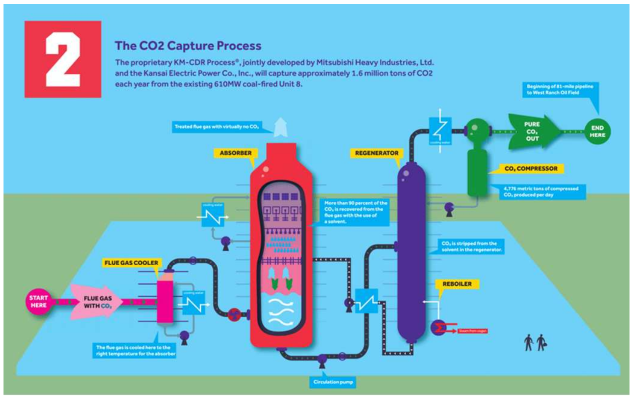

Fig. 4. Schematic representation of the post-combustion CO_2 capture (PCC) process of Petra Nova W.A. Parish coal-fired power plant. Processing units and scales illustrate the OPEX and CAPEX. Courtesy of NRG Energy Inc.

1.1. Alternate separation or regeneration methodologies

GC has always strived to improve the energy or atom efficiency of chemical processes. Currently all solvent-based technologies are regenerated by sending a "CO_2-rich" solvent into a stripper (desorber) where the solvent is renewed (and CO_2 is released) using thermal energy in the form of steam produced from the power plant's boiler (Fig. 4). The heat provided to the stripper is often broken into three separate pieces: sensible heat to bring the stream of rich amine up to the operating temperature of the stripper ($Q1$); enthalpy of reaction to reverse the CO_2 absorption ($Q2$); and heat to vaporize water in the stripper to drive the desorption reaction forward by removing CO_2 as it is released from the stripper ($Q3$). A wide range of creative concepts have been attempted to lessen this energy required for regeneration by either reducing the *amount* of material to send to the regenerator (which affects $Q1$ and $Q3$), or by *offsetting* the heat of absorption/desorption, (which affects $Q1$–$Q3$). Alternatively, the use of nonthermal energy sources has been explored, such as chemical, mechanical, and electromagnetic energy. We note that each of these concepts is still being tested at the laboratory scale and has yet to be demonstrated at a large scale.

1.1.1. Offsetting the heat of absorption/desorption. Reduction of the enthalpy of CO_2 absorption by sole means of molecular design of the solvent structure can be achieved. The irony of solvent development lies in the strength of the solvent, *i.e.,* its chemical affinity toward CO_2. One would think that the most logical way to make CO_2 capture more efficient would be to design a solvent that has a low binding enthalpy with CO_2 or, in a perfect world, thermo-neutral capture. This, as it turns out, is not feasible and is a misconception that has been refuted by the work of Mathias.[16, 17] Mathias identified the optimal thermodynamic range for CO_2 capture solvents, describing a "Goldilocks'" range, with solvents having −60 and −70 kJ/mol binding enthalpy being just right. The reason for this range is simple, and it comes down to the optimal CAPEX and OPEX of a working process. Solvents with low enthalpies and high CO_2 partial pressures would require more solvent, higher solvent recirculation rates, and in turn, increased reboiler duties and pumping costs. Conversely, solvents with a high enthalpy of solution and low CO_2 partial pressure would entail a high reboiler duty to release CO_2 from the solvent, and could suffer from higher rates of oxidative and thermal degradation. We note that Rochelle has argued for higher heats of reaction to provide a high degree of thermal compression of CO_2, to save on energy requirements for mechanical compression of CO_2 to a supercritical state, though these benefits may be limited to only *aqueous* amine solvents.[18,19,20] Thus, we emphasise that solvent selection should aim to minimise the CAPEX and OPEX of the entire process. To maintain the objective of 90% efficiency and productivity, solvents with low heats of reaction require increased solvent flow rates and/or flue gas chilling, resulting in cost trade-off.

Some approaches have focused on offsetting the enthalpy of absorption/desorption of CO_2 with the heat of a concomitant physical (fusion or melting of the sorbent) or competing chemical phenomenon (Fig. 5). Brennecke *et al*. have demonstrated the former concept with a solid sorbent undergoing an endothermic phase change (melting) as it picks up CO_2 and the heat of fusion (solidification) as CO_2 is released.[21] Leclaire *et al.* have shown that the sub-stoichiometric amounts of an organic additive that compete for the reversible binding of the solvent lead to both an increase in cyclic capacity and a 30% reduction of the global stripping load ($Q1 + Q2 + Q3$).[22] In both cases, CO_2 fixation is no longer conducted through an addition but a substitution reaction scheme. This shift of molecular paradigm allows tuning of both the enthalpy and entropy of the absorption/desorption processes. Although both parameters generally compensate for each other,[23] such a strategy allows significant modification of the CO_2 binding isotherms (see next section) and partial escape from the heating/pumping-cooling trade-off.

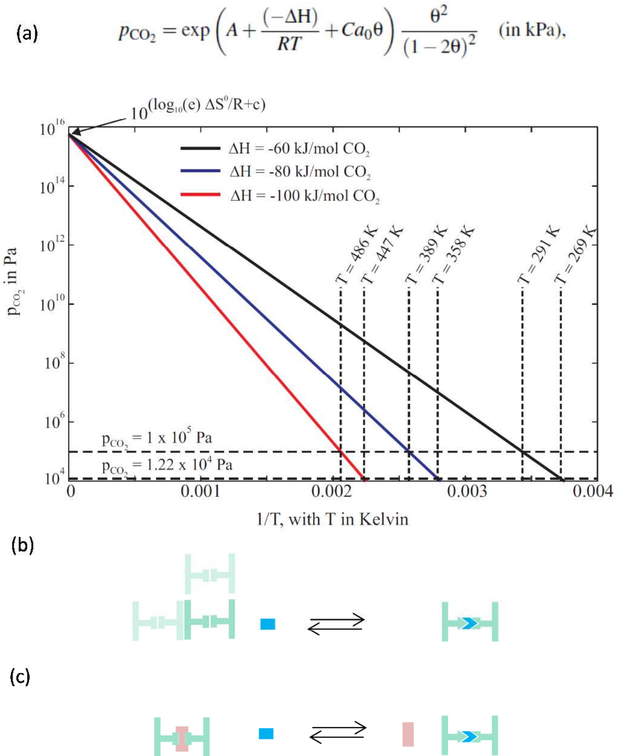

Fig. 5. Offsetting the enthalpy of absorption through physically or chemically competing processes. (a) Relationship between binding entropy and enthalpy and the isotherms. θ: solvent loading, a_0 is the initial concentration of amine; $A \propto \Delta S^{0*}/R$, a measure of the overall change of entropy associated with the process of dissolution and absorption; $C = -7.187$[24] Schematic representation of the physical (b) and chemical (c) competing strategies (green : basic absorbent; blue : CO_2; red : acidic competitor) .

Another strategy focused on shifting the free energy of solvation of ions to destabilise the CO_2-containing ions in what is defined as a polarity-swing-assisted regeneration (PSAR).[25] PSARs have been shown to drop the reboiler temperatures by as much as 73 ˚C to release the same amount of CO_2, allowing for lower-grade heat to regenerate the solvent, though we note PSARs are currently limited to switchable ionic liquid solvents. All of these strategies are supplemental to thermal heating, primarily achieving efficiency gains by reducing the amount of material to heat or the temperature required to release CO_2 (see Section 1.1.2.).

1.1.2. Reducing the *amount* of material sent to the regenerator. The great architect Ludwig Mies van der Rohe once stated “Less is more.” Taking inspiration from that quote, the most obvious way to reduce the regeneration energy is to reduce the *amount* of material sent to the regenerator. The easiest way to envision this is promoting rich/lean phase separation, where only solvent loaded with CO_2 is sent to be regenerated. Below are a few concepts that focus on reducing the amount of material sent to the regeneration column.

There have recently been imaginative CO_2 release strategies supplemental to thermal heating that have been proposed to increase efficiency of third-generation solvents. Such regeneration strategies include phase changes or pre-concentration of the CO_2-rich solution to minimise the amount of material delivered to and heated in the stripper (regeneration column). There are a handful of reports of phase changes as a means to concentrate the CO_2-rich form of the solvent, reducing the amount of material sent to the regenerator (reboiler) and thus there is less mass of material to pump, heat, and cool.[26,21, 27, 28, 21, 29] Phase-change chemistries have been attempted by notable groups Perry *et al.* (GE Global Research) and Broutin *et al.* (DMX process at IFPEN), who have shown that concentrating the CO_2-rich solvent can reduce heat duties significantly.[30] There has been a recent surge in R&D efforts on “water-lean” solvents, which aim to achieve efficiency gains by minimising the amount of water needed in the solvent. Reducing water to <10 wt% projects reboiler (regenerator) heat duties that are 40% lower than those for aqueous solvents.[31] Further, removing water as a carrier solvent introduces unique physical and thermodynamic properties that researchers are investigating as means of efficiency gains. We note that none of these solvents are commercialised, and they are still undergoing significant R&D efforts to be commercialized.[31]

With those examples demonstrated, we take inspiration from notable GC approaches to search for other methodologies that could be used to lower the regeneration energy.

Some groups have demonstrated phase-change catalysis using magnetic particles.[32] Could a magnetic separation be performed in which CO_2-rich material can be designed to be magnetic, so it could be concentrated by a magnetic field? A magnetic separation opens new doors for use of concepts such as magnetic pumping in lieu of mechanical pumping or use of thermomagnetic convection to promote more rapid heat exchange.[33]

Researchers have developed green synthesis and catalytic processes using thermoregulated separations[34] that proceed only in a specific desired temperature range where reagents are miscible. If the temperature gets too high or too low (*i.e.*, runaway reaction), the reagents phase-separate and the reaction shuts down. Upon heating or cooling back to the desired range, the reagents would redissolve and the reaction could begin again. We envision that CO_2 capture solvents could be designed as smart solvents that use thermoregulated solubility to promote phase changes or concentrations of the CO_2-rich solvent. We have yet to find examples of thermoregulated solvents in the literature, but we emphasize such systems remain at least plausible for CCUS. We also suggest that such systems could be developed for other gases critical in the energy industry, e.g. H_2 or O_2 for syngas and oxy-combustion respectively.

We also question whether separations could be performed using changes in density. Unlike water-based solvents, where the CO_2 carrier is dissolved in 70 wt% water, in concentrated water-lean solvents, the CO_2-rich forms are about 10% more dense than their CO_2-lean forms.[35] Thus, we ask whether differences in density could be exploited to concentrate CO_2-rich solvents to send less material to the absorber. High gravity (High-G) columns have been looked at[36,37] as a means to improve mass transfer, though they could be used as a means to concentrate the CO_2-rich form of the solvent prior to pumping into the regenerator. In addition to reducing the heat duty from regeneration, such concepts could also provide secondary boosts to efficiency: CO_2-lean, *i.e.,* regenerated solvent could be pumped back to the top of the absorber but also serve as an intercooling fluid to offset temperature bulges (due to the exothermicity of chemical-based CO_2 capture) in the absorber.

1.1.2. Employing alternative heat sources and delivery systems (toward reducing CAPEX). Because all regeneration methods require heat energy, one expects that the efficiency of regeneration could be improved by the use of alternative methods of delivering heat. Power plants have been designed with sufficient heat integration that all realistically accessible heat is already recovered and used. We point to potential innovations in use of alternate heat sources or new methodologies to deliver heat.

Recently, alternative heat delivery systems have been proposed to improve the efficiency of solvent regeneration. Heat pumps have been assessed for their viability to pump heat from ambient sources to power CCUS infrastructure—more specifically, to regenerate the solvent.[38,39] Liu *et al.* claim heat pump integration into aqueous monoethanolamine (MEA), claiming a questionably low 1.67 GJ/tonne CO_2 captured,[39] which is claimed to be over 20% more efficient than CANSOLV (2.3 GJ/tonne).[14] Similarly, dielectric heating, *i.e.,* microwave irradiation, has been studied as a means to aid in regenerating aqueous solvents. There have been few studies on microwave-assisted regeneration on solid sorbents,[40-43] though the technique is not prominent for solvent-based regeneration. Fan *et al.* have shown microwave-assisted regeneration of aqueous MEA at lower temperatures (70–90 °C).[41] We note that these studies are predominately at the laboratory scale and have yet to be validated by larger-scale testing and modelling. Further, we note these numbers are quite speculative and require an apples-to-apples comparison with conventional regeneration methodologies. Such a comparison would require these systems to be assessed on a total equivalent work basis and compared against known systems[44] for any meaningful conclusion to be made. In any case, we present them as interesting concepts and options that can inspire alternative sources of heat or heat delivery systems that could be used to reduce the CAPEX and OPEX of solvent-based CO_2 capture.

Regeneration methodologies other than solely thermal heating have been investigated. Examples of alternative regeneration include the creative electrochemically mediated regeneration (EMAR) by Hatton *et al.*,[45] which uses electrical energy to release CO_2 at room temperature but at elevated pressure, saving on mechanical compression costs. Another concept involves using photothermal heating using carbon-black nanoparticles to absorb UV-VIS light.[46] Such systems allow for the use of renewables to provide regeneration, albeit intermittent, of solvents. Lastly, acoustic regeneration using ultrasonication has also been proposed as a means to regenerate aqueous[47] and water-lean solvents[48] in lieu of thermal heating, though to our knowledge such acoustic systems have yet to be proven successful beyond a laboratory scale.

1.2 Changing thermodynamics of capture

Through millions of years of Darwinian evolution, nature has managed to generate an optimised biomolecular system that can perform highly efficient and cost-reduced gas purification. The technology equipping the respiratory systems of almost any organism, from animals to plants, fungi, and bacteria is based on the ubiquitous haemoglobin molecule. If we consider the work of respiration by living creatures, which consists of double antiparallel capture, the transportation and delivery of dioxygen and carbon dioxide uses around 0.35 J/L for a healthy adult human organism, *i.e.,* 0.27 GJ/ton of O_2/CO_2 which are simultaneously processed.[49] The key to this modest OPEX, which is ten times lower than what is required by current state-of-the-art PCC systems, is the allosteric cooperativity of the gas absorption and desorption chemistries.

Positive cooperativity, which arises from the favourable interplay of interactions within a multivalent system, favours the extreme loading states (all or nothing),[50] and consequently provides symptomatic sigmoidal binding isotherms. Gaseous targets may consequently be efficiently captured in isothermal conditions through simple pressure swing, as haemoglobin does. Alternatively, if thermal swing is envisaged (Fig. 7d and e), working capacity may be significantly increased with respect to traditional non-cooperative systems. Cooperativity factors of the many multivalent sorbents (Fig. 6a), which have so far been studied mainly for their increased loading capacity, should be screened. Interestingly, cooperativity in CO_2 binding can and does generally arise from intra- and/or intermolecular structural transitions: recent studies on solid sorbents showed that cooperative CO_2 fixation between neighbouring binding sites is assisted by an induced fit of the lattice (Fig. 6b). In solution, cooperative CO_2 binding on oligomeric static (Fig. 6c, Esser-Kahn),[51] or self-assembled (Fig. 6d, Leclaire)[22] multivalent sorbents was systematically accompanied by aggregation into a separate liquid or solid phase. This phenomenon, which is directly due to the ionising character of carbon dioxide fixation and was well exploited to design CO_2-switchable molecular systems[52,53] allows to both reduce the energy required for regeneration and minimise the amount of material to be sent into the regenerator.

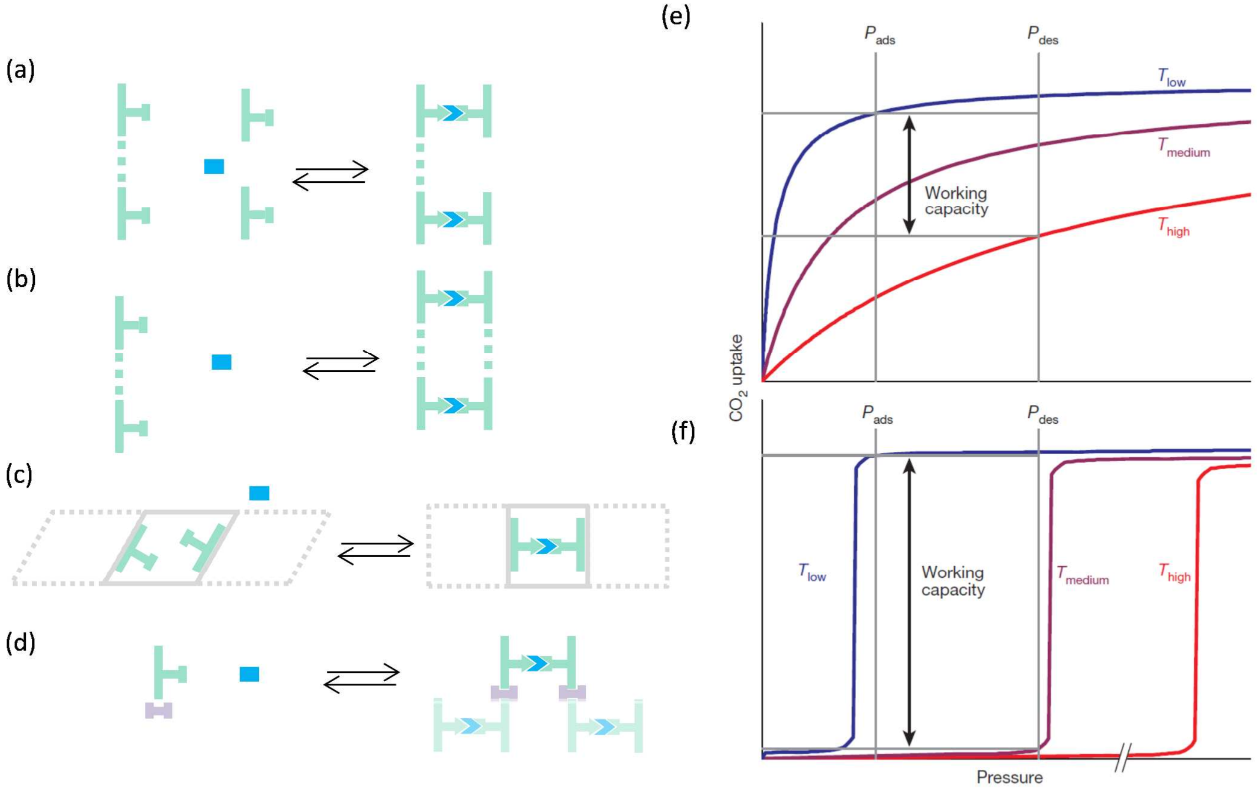

Fig. 6. Schematic principle of CO_2 binding chemistry and the various molecular strategies explored for cooperative binding based on: (a) allosteric binding (b) chelate binding (c) induced fit –coupled binding, (d) self-assembling coupled binding. Green: organic Lewis base; blue: CO_2: purple: CO_2-capture agonist; red: CO_2 capture antagonist. (e) Absorption isotherms of a non-cooperative capture agent. (f) Idealised absorption isotherms from a cooperative capture agent.

1.3 Changing speciation of capture

Opposites attract. CO_2 is a linear molecule that is sp hybridised with a weakly electrophilic central carbon atom. Currently, all chemically based CO_2 capture has been performed using liquid or solid Lewis-Brønsted base couples (Fig. 7a). There have also been some clever cases of Lewis acids, *i.e.,* frustrated Lewis pairs (FLPs), which bind CO_2 through an oxygen, though they are not likely to be used in hydrated gas streams due to their sensitivity to water (Fig. 7b).[54, 55] Lewis and Brønsted bases proceed via electrophilic attack on the central carbon of CO_2. Regardless of formulation, nearly all chemically based solvents capture CO_2 via nucleophilic attack by water, or alcohol or amine moieties, in the process rehybridising CO_2 from linear sp to trigonal planar sp^2 anionic carboxylates (carbamates, alkylcarbonates, azoline-carboxylates), which are all very similar in structure and properties (Fig. 7).[31]

1.3.1. Hot (proton) potato*:* proton (de)localisation. The bond formation and dissociation trade-off is directly related to the enthalpy and entropy of the CO_2 fixation process and greatly affects the physical properties of the resulting adducts. Some research groups have already shown the benefit of changing the acid/base equilibria of solvent-based capture chemistry. CO_2 reacts with either water, amines, alcohols or thiols and may form a carbonic, carbamic, alkylcarbonic, or alkylthiocarbonic[56] acid, which will be in equilibrium with their corresponding conjugate bases: bicarbonate, carbamate, alkylcarbonate, and alkylthiocarbonate, respectively (Fig. 7a). In the case of water-lean solvents, ion pairs have been shown to aggregate and salt up the solvent, which in turn increases viscosity and reduces the rates of mass transfer and heat exchange.[57,58] Cantu *et al.* have demonstrated that in some water-lean solvents for alkylcarbonate and carbamate systems, the chemical equilibrium can be shifted to result in a higher population of neutral “acid” forms of captured CO_2.[59]

Essentially, the base and acid sites end up playing “hot potato” with the proton. Having a higher proportion of neutral acid forms of captured CO_2 can reduce the ionicity of the solvent, in turn reducing viscosity and thereby improving heat exchange.

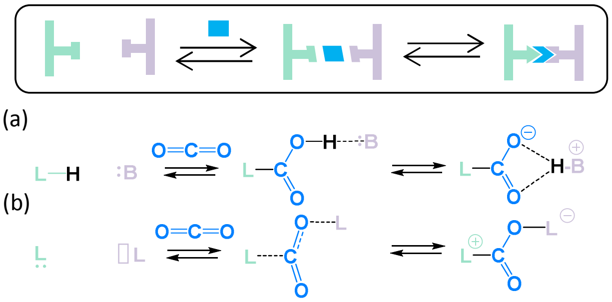

Fig. 7. Proton and charge localisation affecting chemical and physical properties of CO_2 capture systems. (a) Lewis base (green L) and Brønsted base (purple B) of (b) FLPs (green L: Lewis base; purple L: Lewis acid)

Using the principles of GC, we question whether chemists could fine-tune the equilibria to promote exclusively 100% neutral capture by reconfiguring the solvation free energies of acid and ion pairs in solution.

1.3.2. Hot potato #2, electron (de)localisation. If proton localisation may play a central role in the physical and chemical features of capture processes based on Brønsted Lewis base pairs, charge (de)localisation may also be a key for frustrated Lewis pair-based capture system. Frustrated Lewis pairs are couples in which steric congestion precludes neutralisation, which will occur when CO_2 is incorporated as a spacing unit (Fig. 7b).[54] This steric mismatch can indeed be exploited to destabilise the starting mixture. Whereas the overall thermodynamics and reaction rate was recently proved to be determined by the strength of the Lewis acids,[60] the electronic features of the Lewis base will greatly affect the binding/loading capacity, as recently shown by Wang and colleagues.[61] From these statements, it appears that the optimised design of FLPs with the focus on the electronic features of each partner may lead to high capacity systems with low regeneration enthalpies.

1.3.3. Two for the price of one. We have long heard advertisements proclaiming that “more is better.” Thus, we question whether there are means to design a capture solvent that can complex more than one CO_2 per active site. Chemically selective solvents chemically react with CO_2 at a single active site (i.e., degree of alkalinity), making one equivalent of ions in solution. The challenge, of course, is how to do this.

Phosphorous and nitrogen are trivalent elements; loading capacities of nitrogen or phosphorus bases may theoretically increase when their degree of substitution decreases. One may argue that the binding of a second CO_2 molecule on a monocarbamate/carbamic acid may be greatly hampered by its poor nucleophilicity and that the electronic repulsion may be too strong to obtain a stable 2:1 adduct. Yet synthetic chemists have proved that diimide can be formed and even used to capture not one but up to two molecules of CO_2 (Fig. 8a). They also have shown that ever-increasingly hindered amine can be isolated as stable species.[62] Early kinetic studies performed by Monsanto in a perspective of using CO_2 as a green substitute for phosgene for the production of polyurethanes gathered convergent evidence of the formation of 2:1 CO_2:amine adducts in the presence of bulky nitrogen bases (Fig. 8b). This finding was later confirmed by *in situ* nuclear magnetic resonance analyses performed by Kortunov *et al.* at ExxonMobil,[63, 64] and raises the question of protonation state of this pseudo-malonic species whose carbon-based analogue is known to be stabilised as a monoanion.

The concept of branched linear homo- or block oligomeric CO_2 capture may not seem far-fetched. One such di-carbonate (Fig. 8d) was proposed by Baek *et al.*,[65] though there remain questions of whether such species was correctly identified. Taking inspiration from this “CO_2-acetate-anhydride,” we hypothesise that if two molecules of CO_2 could be captured per one degree of iconicity (Fig. 8c and d), solvents would be able to halve the number of ions in solution, lessening the viscosity and heat exchange problems identified above. Further, such a strategy could conceivably double the amount of CO_2 captured in solution, which could improve the atom economy and energy efficiency of the process, by reducing the amount of solvent needed and in turn lessening the power requirements for solvent circulation. It is unclear whether the second CO_2 captured would be more labile than the first, and whether or not the two would be released concurrently or in two different steps. In either case, outside-the-box thinking with respect to changing the speciation of CO_2 could provide substantial efficiency gains for solvent-based processes.

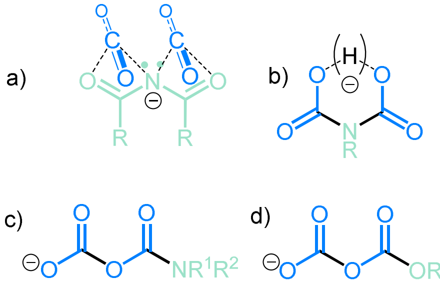

Fig. 8. Two (CO_2 molecules) for the price of one (charge). Conceptual monoanionic (to be confirmed) polycarbamates and carbonates (CO_2-anhydride) showing two moles of CO_2 captured per mole of iconicity: a) alkylcarbonate anhydride; b) carbamate anhydride.

Looking at chemical functional groups that contain two CO_2 molecules, we gain inspiration from GC’s advancements in the field of CO_2 polymerisation with epoxides to produce polycarbonate polymers.[66-71] Obviously, there is not enough epoxide to react with all of the CO_2 being captured, but we question whether an initiator could be designed to polymerise or oligomerise CO_2 into polymeric versions of the dimers shown in Fig. 8. If such a system could be developed, then multiple CO_2 molecules could be captured on a single charged site, producing oligomeric or polymeric CO_2 as a means to increase capacity.

We finally question whether it is possible to change the method of CO_2 capture by changing the speciation of CO_2 when it is captured. CO_2 is an "acid gas" and has nearly unilaterally been captured by means of a Brønsted base. We ask whether it is possible to fight fire with fire: whether or not *Brønsted acids* could be used to chemically react with CO_2 and capture it as carbonic acid. There have been a handful of studies on the solubility of CO_2 in acids[72] suggesting CO_2 is sparingly soluble in acids at standard temperature and pressure, but there are limited studies of solubility at higher temperatures and pressures. If CO_2 can be made more soluble in acids, the concept may not seem as far-fetched. Consider that H_2SO_4 has lower vapour pressure than the amines and physical solvents currently used, is made cheaply and at the scales needed for CO_2 capture. Further, H_2SO_4 is inflammable, and can dissolve SO_x and NO_x conceivably negating the need for selective catalytic reduction (SCR) and flue-gas desulfurisation (FGD) units. Further, from a life-cycle analysis, concentrated acids would remove some significant problems of solvent-based processes, primarily solvent degradation, oxidative and thermal, the formation of carcinogenic nitrosamines, aerosols and heat-stable salts that deactivate organic (see basic) capture solvents. The obvious drawback would be the high acidity of the acid and the challenge and costs of using acid-tolerant infrastructure, though we note that all solvent-based capture formulations are themselves highly corrosive (basic), so the need for any specialised infrastructure with different corrosion resistance may be a moot point.

1.4 From bio-inspired to biochemical capture

Using biological systems as they have evolved to capture and convert CO_2 is smart and an obvious means to promote CCUS thus it does not need coverage here. We emphasise that new areas that focus on methods of rewiring biology for CCUS may have the most value moving forward.

We question whether extremophiles could be exploited to promote bio-based CO_2 capture. Black smokers are hydrothermal vents deep on the ocean floor (Fig. 9). These vents heat the surrounding water to hundreds of degrees centigrade, though the water does not boil due to the immense hydrostatic pressures of the water at these depths.[73] One would expect these vents to be barren landscapes, yet they are home to vibrant ecosystems that have adapted to thrive under these extreme conditions.[73] Black smokers are home to strains of chemotrophs that have been shown to feed off of CO_2 from the vents, using H_2S emitted from the vent as a reducing agent to make carbohydrates via chemosynthesis.[74, 75] If extremophiles such as these can capture and convert CO_2 at these conditions, we should be looking at using these natural systems for hot gas cleanup. Could these cyanobacteria can be used directly, or their enzymes isolated and used directly in a hot absorber or reboiler to facilitate CO_2 uptake or release?

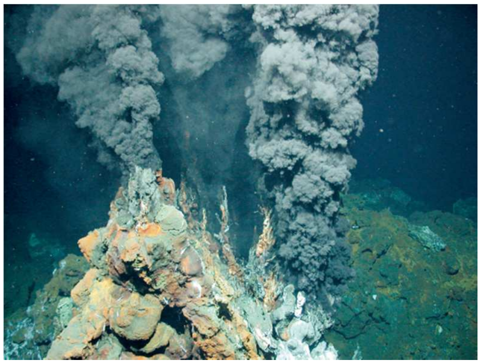

Fig. 9. Black smokers (hydrothermal vents) at the bottom of the ocean have created ecosystems with extremophiles that thrive at high temperature and pressure. Image from World Ocean Review.

2. Head #2. CAPEX materials and intensification

The second head of the CCUS hydra is the infrastructure required to separate CO_2 from mixed gas streams—the CAPEX. The capital costs of infrastructure needed to perform CO_2 capture are substantial. Installation of a bolt-on retrofit to a single medium-sized 550 MW subcritical coal-fired power plant is projected to cost on the order of $500M USD.[11] The high CAPEX of CCUS technologies is primarily due to the size and cost of the absorber (where CO_2 is absorbed), heat exchangers, stainless steel piping and pumps, and the cost of the CO_2 capture solvent. These capital investments have to be recovered by the power station, who in turn raises rates and projects the cost onto consumers, who now pay more for electricity. *Strategy for Head #2: Reduce equipment size via decreasing the size of infrastructure or using cheaper materials and manufacturing processes and more facile synthesis.*

2.1. Enhanced absorption concepts

Size matters. The first strategy to reduce the costs of CAPEX is to reduce the size of the infrastructure. The costliest unit of solvent-based technologies is the absorber column. Absorber size is directly linked to cost, and size is linked to the rate of mass transfer of CO_2 into solution. If CO_2 could be absorbed faster, equipment sizing could come down proportionally.

We take inspiration from The Fonzie, who was known to keep cool. CO_2 appears to move differently in organic liquids than in aqueous ones. Whyatt *et al.*[58, 76] had shown mass transfer is fast in organic solvents, albeit at viscosities that are orders of magnitude higher.[57] Further, observe an inverse in mass transfer with temperature, indicating the solvents can absorb *faster* the *colder* absorption is performed,[58, 76] which is counterintuitive from aqueous solvents. Their work suggests viscosity may not be a problem for mass transfer, though it will still need more heat exchange and energy for pumping. We suggest that such a finding can be exploited, and engineers could consider configuring absorption to be performed below 40 ˚C, which is often the standard absorption temperature.

Running colder could increase the absorption rate due to an increase in concentration of CO_2 physically dissolved in solution, which would drive liquid kinetics, enabling smaller/cheaper absorbers and lower solvent circulation rates. Running colder would require cooling or refrigeration, though the energy requirements could be offset by a reduced reboiler duty, because cooling the flue gas would condense water out of the gas prior to its accumulation in the solvent.[35]

A second strategy for reducing equipment size via increased absorption rate is to use catalysis for the absorption process. There have been recent efforts using biological or chemical catalysts (inspired by carbonic anhydrase) that tolerate high temperature, and organic media may help to improve the kinetics of CO_2 capture and release.[77, 78] Other strategies have involved mimicking the active site of the enzyme, using Zn^{2+} catalysts to enhance the rate of CO_2 hydration ($CO_2 + H_2O \rightarrow H_2CO_3$) or release.[79, 80] While these methodologies have been shown to increase the rate of absorption, they are unlikely to provide any further gains as the CO_2 uptake will still be mass transfer limited by the low solubility of CO_2 in water.

We postulate that there may be ways to alter the gas/liquid interface of capture solvents to enable facile diffusion of CO_2 into the fluid. Can we change the gas/liquid interfaces to be more reactive or more gas permeable? Can we take inspiration from CO_2 as a stand-alone green solvent, either as supercritical CO_2 in CO_2-expanded liquids[81] or organic/aqueous blends (organic aqueous tunable solvents, or OATS).[82] Such studies on CO_2-expanded liquids has shown an increase in solubility or diffusion of other gases such as H_2,[81] so we ask whether we can we apply similar principles of gas-expanded liquids or other means to promote better/faster mixing or gas dissolution? Surfactants can be used to change the interfacial structure and solubility/mixing of reagents at the interface; are methods available for placing CO_2-philic surfactants at the interface that can be used to favourably dissolve CO_2? It has been shown that there is high solubility of CO_2 in the ionic lattices of ionic liquids.[83] We postulate that porous interfaces or porous liquids could be designed with channels or pores to favourably solvate and diffuse CO_2 more rapidly than in aqueous solvents. Any of these strategies could be used to increase mass transfer and, in turn, reduce solvent circulation rates and equipment size, reducing both CAPEX and OPEX.

2.2. Enhanced desorption concepts

Another strategy to reduce CAPEX would be the use of simpler regeneration configurations or smaller infrastructure. The stripper is another large costly unit of infrastructure with varied configurations having varied costs.[84] Other elements of cost, include the heat exchanger (cross-exchanger), circulation pumps, and amount of solvent used, can directly affect the costs of any viable process, though desorption has a smaller effect on CAPEX.

All commercial first- and second-generation solvent technologies release CO_2 thermally from aqueous solvents by heating above 100 ˚C with steam from the power plant's steam cycle. Similarly, third-generation water-lean solvents also use thermal regeneration, though regeneration temperatures have been shown to be as low as 88 ˚C, which would allow lower-grade heat sources for regeneration, providing efficiency gains.[25, 35] There have been studies of the costs of different (what we would call conventional) stripper configurations common to aqueous solvents (*e.g.*, multi-pressure, split stream, vapour recompression), but the costs vary within a few percent at best, because each configuration is at best a slight replumbing of the process. [84] Thus, there is a need for GC to explore the design and feasibility of innovative regeneration methodologies with lower costs.

Sadly, we have yet to find something as simplistic as a pipe to space that can suck all of the CO_2 out of the air or a capture solvent. This however, has not prevented us from envisioning some *avant-garde* concepts (Fig. 10) as a means to reduce CAPEX. As mentioned before, CAPEX reduction on the desorption side may not come from a new stripper configuration, but might have to come from inventive concepts to facilitate CO_2 release.

Fig. 10. Advanced desorption concept; space vacuum as inspired by Brooks *et al.*, "Spaceballs," 1987.

The first concept can simply be the rate at which CO_2 can be stripped from the fluid. We have previously highlighted attempts to get CO_2 into solution faster by means of catalysts, but there are limited studies on catalytic CO_2 release. Leclaire *et al.* have recently proposed evaluating the potential use of carbamates in hydrometallurgy to design sustainable metal purification processes.[85] While the use of oxo- or aminophilic metals may strongly alter the thermodynamics of the CO_2 capture/release chemistry and thereby affect the OPEX, it may also modify its kinetics for release, in turn potentially shrinking the size of the stripper. To go a step further, one can imagine that lean/rich–metal self-sorting may be used for the concomitant purification of CO_2 from flue gas and metals from waste material, thereby allowing pooling of the CAPEX and OPEX for convergent CO_2 and valuable metal capture.

A second concept to reduce CAPEX could be to improve heat transfer, thus shrinking the cross-exchanger. Water is a good conductor of heat, but nearly all third-generation solvent technologies use organic solvents, which have half the thermal conductance of water. The lower the rate of thermal conductance of the solvent, the larger and costlier the cross-exchanger becomes. As described above, having a metallic-rich fraction may increase thermal conductance, thus enabling third-generation solvents to have comparable (potentially smaller and cheaper) strippers and cross-exchangers to aqueous amines. If a potential effect on solvent degradation is also to be expected, metal additives may be a promising track to envisage facilitated stripping additives and process configurations.

A third concept of reducing CAPEX would be to coax CO_2 out of solution by manipulating physical conditions in the stripper. Andarcia proposed the use of "stripping aids" to reduce the partial pressure of CO_2 over the solvent, acting as an artificial vacuum to coax more CO_2 out of solution at a given temperature.[86] This concept is similar to the way steam strippers work, in that the steam in the stripper reduces the partial pressure of CO_2, forcing it out of solution. In this case, these volatile stripping aids could act in concert with steam to reduce the partial pressure of CO_2 even more or facilitate a faster release of CO_2 during stripping. Granted, the introduction of VOCs could hardly be considered green, but we highlight that the concept could be made greener if the stripping aid was nontoxic, bio-sourced and nonflammable, as the aid would be recovered during the CO_2 compression step, where cooling would condense and recover the stripping aid with any water vapour.

2.3. Innovative and integrated processes

Because CCUS involves both chemistry and engineering, we highlight the need for innovative integrated processes that may achieve efficiency or cost gains by inventive CCUS operations or by using stranded renewable resources that have no large-scale storage options available.

2.3.1. Turn it up to 11. Solvent-based CO_2 capture units are large pieces of infrastructure that were envisioned to operate at a constant circulation rate to capture the consistent emissions of CO_2 from coal-fired power plants. This is because real-time adjustments to change steady-state operation are difficult and could introduce new risks and potential failure of the capture unit. The reality is that power plants cycle capacity to meet demand; thus, the rate of CO_2 emissions changes with the load cycle to the plant. Arce *et al.* were the first to address this issue and proposed an innovative process concept of flexible solvent regeneration to minimise costs of CO_2 capture.[87] In this study, a 30 wt% MEA solvent was modelled to intermittently regulate the extent of solvent regeneration to minimise operational costs. In this study, they adjusted the lean/rich loading to buffer and adapt to periods of high and low load. In periods of high power demand, the capture solvent was allowed to continually increase its rich loading, allowing more steam to produce power to export to the grid during peak hours when demand and cost of power are high. Conversely, in periods of low power demand, the solvent could then be regenerated to a leaner solvent loading when power is more abundant, and costs are lower. Further, their modelling findings suggest efficiency of the plant could be increased by as much as 10% using this type of flexible approach. We find it encouraging that flexible operation of a pilot-scale power plant is feasible in that perturbations in plant operation could be handled and that power plants could adjust to gradient changes in lean/rich solvent loading with minimal impact.

2.3.2. Digging deeper. Alternatively, Rochelle[18] and Davidson *et al.*[88] have looked at using geothermal resources for regenerating amines. Davidson's study focused on the viability of direct-use geothermal resources *directly under* coal-fired power plants.[88] The aim of this study was to see the cost and energy output for stranded geothermal resources in direct-use CCUS applications. Hot, compressed water (<150 ˚C) can be found anywhere in the subsurface pending the depth required to reach it. These resources are everywhere, though they are not utilised as the water does not efficiently power an organic Rankine cycle (ORC) turbine to justify their cost. In this study, Davidson and team focused on assessing the costs and power output for using hot, compressed water for direct-use applications in CCUS infrastructure such as boiler feedwater preheating or powering a reboiler to regenerate solvents. They concluded that 550 MW scale subcritical power plants could use these resources for boiler water preheating, saving 19 MW of power for boiler feedwater preheating only, requiring 20,441 liters per minute (lpm) of 150 ˚C water at a cost of $34.7M USD. For comparison, that flow of water would produce only 9 MW of power in an ORC at a cost of $47.2M USD ($5.2M/MW). Powering the entire reboiler for MEA could produce 101 MW of power, though it would require a prohibitive 265,000 lpm at a cost of $108.6M USD ($1.1M/MW). Third-generation solvents like CO_2BOLs, however, were projected to make 121 MW of power, requiring a sizable, but not unreasonable, 75,700 lpm to regenerate the solvent at a cost of only $51.6M USD ($0.42M/MW).[88]

With the two examples above, we question whether or not there are other innovative or integrated processes that could be developed. Another area of need is the compression of CO_2; mechanical compressors consume as much as 12% of loss of efficiency for a power plant to compress CO_2 to a supercritical state for pumping or sequestration.[89, 90] There have been investigations into varied compression strategies, ranging from multistage compression with intercooling, compression combined with liquefaction and more exotic methodologies such as supersonic shockwave compression.[91] Similarly, Rochelle (UT Austin) has shown that thermal compression of CO_2 requires lower compression work than mechanical compression and thus a lower total equivalent work needed for carbon capture.[92] The trade-off is the requirement to regenerate solvents at temperatures above >120 ˚C, potentially increasing the rate of thermal and oxidative degradation of the solvent. We question whether there could be alternative means of compression, via Hatton's EMAR concept,[45] or by integration with other chemical or mechanical processes such as solar-thermal compression or more *avante garde* concepts using things like thermoacoustic engines.

2.4 Co-capture

An old adage said you can get two birds with one stone. CCUS involves more than just CO_2 capture; there are units of operation to capture SO_x, NO_x. SO_2 is extremely electrophilic and is known to make Lewis adducts with even weak nucleophiles, while NO_x are radical gases, which can oxidise or convert some amines into carcinogenic nitrosamines.[93, 94] These heat-stable salts (HSS) that form between NO_x and SO_x in aqueous solvents[95 Aerosol and Air Quality Research , 14: 550–558, 2014] cannot be thermally regenerated. Thus, HSS have to be recovered and reactivated via processes such as ion exchange;[96] otherwise, the solvent must be disposed of as organic waste. To negate solvent deactivation or destruction, emissions treatment requires two additional units of operation prior to any CO_2 adsorption. The first unit is SCR to remove NO_x, while the second unit is an FGD unit for removing SO_x. Each unit reduces the accumulation of NO_x and SO_x to ppm levels, though at the scales of CCUS, this still translates to tonnes per year of waste, of each, per power plant. If a solvent could perform co-capture, a smaller all-in-one unit or two units rather than three separate ones would save on waste, manufacturing and equipment costs, and energy requirements, as well as space on the skid, greatly reducing CAPEX and the solvent inventory required for each separation.

Some aqueous formulations (CANSOLV) and water-lean solvents have been shown to exhibit reversible SO_x capture via alcohol (alkyl sulphite)[97, 98], amine,[99, 100] Imidazole/azole,[101, 102] ethereal moieties.[103] or carboxylates.[104] Thus, it remains feasible that the electrophilicity of SO_2 could be directed to complex to moieties that are not the CO_2-active site (*e.g.*, amine); onto a carbamate or carbonate as represented in Fig. 11a, or alternatively attack an ethereal or alcohol moiety on an alkanolamine as represented in Fig. 11b. We envision such a hybrid solvent would have to load CO_2 first to avoid deactivation of the active site by the more-reactive SO_2. Once loaded, then the CO_2-rich solvent could then be cycled upstream to remove SO_2. Unloading of CO_2 and SO_2 from the solvent could be performed in separate steps assuming the desorption temperature is different for the two gases.

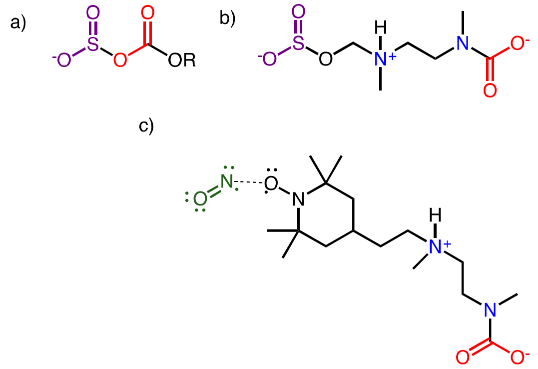

Fig. 11. Proposed conceptual (not yet observed) structures. a,b) co-capture of SO_2 and CO_2. c) co-capture of NO and CO_2.

It is unclear whether a co-capture strategy could be employed for NO_x because they contain unpaired electrons. We postulate that liquid solvents composed of stable radicals like TEMPO [(2,2,6,6-tetramethylpiperidin-1-yl)oxyl] could be designed to reversibly complex NO_x (Fig. 11c). The viability of such a hybrid system is questionable; there are many unknowns of the stability of radicals in concentrated organic solvents, and to our knowledge no reversible NO_x capture has been demonstrated. Thus, we propose consideration of this concept as a potential means to reduce solvent requirements or combine units of operation to improve CAPEX.

2.5 Additive manufacturing and materials

Because CAPEX involves more than just the cost of the material, manufacturing can provide substantive reductions in CAPEX. Nature is a grand architect, building exotic and complex systems from simple precursors with minimal waste, which humans have not accomplished. Carbon Capture and Storage (CCS) infrastructure has historically been built using energy-intensive casting, welding, or wasteful *subtractive manufacturing* (*i.e., machining*). Current advancements in *additive manufacturing* have been gaining popularity since the 2000's, enabling manufacturing with potentially lower energy requirements and minimal waste.

Less is more. From a green chemistry and engineering perspective, additive manufacturing is far greener than conventional methods. Building from the ground up allows for less material to be used in manufacturing than does subtractive manufacturing like computer numerical control (CNC) machining. Some groups have begun looking at 3D printing of small components such as column packings (*e.g.*, Heli-Pak, saddle, Raschig rings, balls, and structured). Beyond the small packing, the ability to make structures via printing opens the doors for manufacturing units of infrastructure on site, facilitating transportation logistics while decreasing shipping costs and installation times. 3D printing may also provide cheaper and more structurally sound infrastructure because more complex systems can be designed with greater control over geometry to reduce failure points by reinforcing weak points in critical areas. Other advanced manufacturing techniques such as friction-stir welding could be used to join metals and piping with greater control over weld integrity and metallurgical properties. Friction-stir welding is also modular and could be used to manufacture and assemble infrastructure on site, also reducing costs. Ultimately, we champion advanced manufacturing as an attractive means to reduce CAPEX of CCUS infrastructure, assuming larger infrastructure such as absorber or stripper columns could be printed on site.

Another advantage of additive manufacturing is the ability to mimic nature and manufacture complex systems that could not be made with conventional means. With 3D manufacturing, new exotic packings such as gyroids (Fig. 12a) can be manufactured. Gyroids, discovered by Schoen, have been proposed as more efficient packings and heat exchangers.[105] Gyriods are thin and structurally strong, providing a continuous high surface area packing, with attractive heat transfer, lower pressure drops and uniform film thickness.[106]

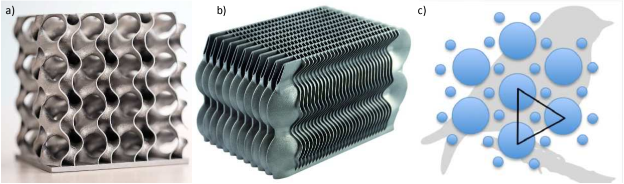

Fig. 12. 3D printed infrastructure. a) bi-continuous packing, b) microchannel heat exchanger, c) artificial lung. Images from: https://www.sglgroup.com, GrabCAD Blog, Credit: ThinkStock/XiaoZhi Lim.

3D printing can also be used to manufacture heat exchangers with microchannels and high surface areas (Fig. 12). Microchannel heat exchangers are more compact and efficient than conventional plate-and-frame or tube/shell heat exchangers, suggesting cost improvements could be gained with units of operation such as the cross-exchanger. Thinking further down the road, more complex heat exchangers such as gyroids can also be used, as their tri-continuous phases could be configured for cold-rich solvent in one direction, with hot lean solvent coming in on the other side. Thus, 3D printing opens new doors for CAPEX reduction if such packing and heat exchangers could be made at scale.

Gas-to-liquid absorption processes require high gas-liquid surface to be efficient. The challenge is that surface area has to be provided by column packings, which provide a nominal size cost burden. To come back to nature's choices, to process the flue gas at flowrates of an average coal-fired plant, given the pulmonary capacity of human lungs (18 L CO_2/h), only 19 m^3 (a small removal van) of pulmonary tissue, though corresponding to an exchange surface area of 25,300 tennis courts, would be required. Thus, from a cost perspective, any increases in surface area above current packing geometries can yield substantive reductions in cost. Researchers are already starting to create biologically inspired systems to improve gas/liquid contact with the highest surface area for getting CO_2 into solution (Fig. 12c). Esser-Khan presented one such example, mimicking avian lungs as more efficient gas/liquid contactors.[107] Such innovative structures had been considered for years, though they could not be manufactured before recent advances in additive manufacturing.

Another area for CAPEX reduction is swapping out the materials used on CCUS infrastructure for cheaper and more durable materials. All solvent-based processes use some alloy of corrosion-resistant steel due to the corrosivity of CO_2 - capture fluids. The costs of steel alloys vary widely, with corrosion-resistant stainless steel far more costly than carbon steel. Steels primarily corrode due to the formation of carbonic acid, which is produced when water hydrates CO_2.[108] All aqueous solvents require high-cost stainless steel to minimise corrosion and degradation of process infrastructure, though water-lean solvents might be able to use lower-grade steels, enabling considerable cost reductions.[109,110]

Joe Camp famously said, "Just because something has always been done a certain way does not necessarily mean it's the best way." Along these lines, we ask why steels have to be used in the first place. If CCUS infrastructure could be made with something more durable and chemically inert like fibre-reinforced plastic, costs of infrastructure could come down substantially. It is our opinion that the only reason steels are still used is that aqueous solvents cannot wet other surfaces like plastics because the contact angle is too high. Water-lean solvents, which are predominately organic, could wet plastics due to their lower contact angles and surface tensions. Thus, we propose the use of plastics (preferably biodegradable, definitely non-halogenated) as a cheaper alternative to steels.

The choice of using plastics in CCUS infrastructure would at first seem counterintuitive to the principles of GC, though we highlight that from a cost and life-cycle analysis, the corrosion of steel releases highly toxic metals like Ni and Cr, which can end up accumulating in the solvent but also the environment. We also point out that solvent (MEA) degradation has been shown by Rochelle and others to be catalysed by metals from corrosion,[111-114] necessitating the use of corrosion inhibitors, which are costly and not environmentally benign. If steels could be avoided, solvent lifetime would be increased, corrosion inhibitors could be avoided, and ultimately the amount of degradation products that can accumulate in the environment would be reduced. Using plastics could yield substantial cost savings as well as some environmental benefits.

Plastics do have an Achilles' Heel: while they are cheap and chemically durable, they are often not biodegradable, and their environmental impact must be considered. Fortunately, evolution has given us a new weapon to fight the accumulation of plastic in the environment: worms! Researchers have recently discovered bacteria in waxworms (caterpillars) that have enzymes that can digest chemically robust plastics such as polyethylene within hours,[115, 116] as compared to the decades it normally takes for plastic to break down naturally. We envision the use of enzymes such as these to break down spent or old plastic infrastructure after use. Thus, from a cost perspective, cheaper infrastructure like plastics will not only reduce the CAPEX of CCUS, but may result in a lower environmental impact than stainless steels over the lifetime of a CO_2 capture plant (~30 years).

One last concept to reduce CAPEX is to find waste and turn it into valuable products. Coal combustion produces a myriad of waste products such as Hg, HCl, NO_x and SO_x, with the latter converted to gypsum and sold for use in cement board. There remains at least some potential for recovery of other by-products for commercial sale. Consider that stainless steel piping in CCUS infrastructure corrodes over time, leaching metals into the capture solvent. CO_2-promoted metal chelation as shown by Leclaire *et al.*[85] could be used to recover metals from corrosion such as Cr, Ni, and Fe and sell them to recoup at least some element of cost. Revisiting the acid capture concept above, HCl,[72] NO_x, and SO_x can be separated using selective anion exchange membranes, with the acids being recovered and sold commercially.

3. Head #3. The life cycle of capture solvent synthesis, lifetime, disposal, and environmental effects

The third head of the CCUS hydra entails contradictions that must be weighed, where we must balance priorities of whether atom or energy efficiency is more vital or whether solvent durability undermines biodegradability. Here, we present the contradictions of solvent development, focusing on the entire life cycle of the solvent, covering the atom and energy efficiency, synthesis (reagents and waste), solvent durability, and cost. *Strategy for Head #3: Use the tenets of GC, after assessing the challenges and contradictions of solvent development.*

3.1. Chemical selection, production

To be or not to be (green)? The first contradiction of solvent development is the choice of solvent itself. In GC, we gravitate toward greener solvents such as water, which is cheap, inflammable, and nontoxic, though water may not be the ideal solvent for CCUS (Fig. 13). The choice of water as a solvent would seem to be the greenest option, though CO_2 is sparingly soluble in water.[117] unless the pH is basic, where CO_2 is hydrolysed and brought into solution as bicarbonate. Thus, the only way to get enough CO_2 into solution is to add 1˚ and 2˚ amines to either react directly with CO_2 to form a carbamate, or a 3˚ amine which slowly captures CO_2 as bicarbonate or carbonate salt. Aqueous amines have been used since the 1930s[13] to capture CO_2, representing all commercial first- and second-generation technologies. One would think that aqueous formulations are optimal from a GC perspective, yet these solvents are limiting by corrosion of steel infrastructure and the sizeable energy inefficiency associated with regenerating the solvent (boiling and condensing millions of gallons of water an hour).[11] Thus, the first contradiction is blatantly apparent; water is a cheap and green solvent for most chemical processes, but the low solubility, corrosion, and energy-intensive regeneration are limiting in CCUS. For these reasons, new third-generation solvents are focusing on reducing water content as a means to improve solubility and energy efficiency, but to also reduce corrosion at the expense of being flammable, and costlier. The trade-off that is occurring in solvent development would at first seem counterintuitive to GC principles—replacing water with non-volatile organic chemicals—though we argue that this might be a necessary evil.

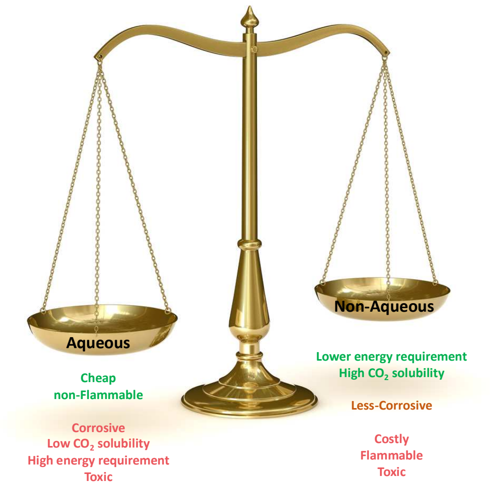

Fig. 13. Solvent selection is a delicate balancing act. Pros and cons of aqueous vs. non-aqueous solvents.

We next highlight the sheer magnitude of solvent needed for separations: millions of kg of solvent are needed *per* power plant! A single 550 MW subcritical coal-fired power plant circulating MEA is projected to circulate over 4,000,000 kg/h of solvent, plus solvent makeup rates.[11] With thousands of coal-fired power plants in the world, the amount of solvent needed for CO_2 capture is overwhelming. We highlight the work of Bara, who first shed light on this bottleneck of chemical production capacity to manufacture simple solvents.[118] Bara cautions that there is not enough capacity to manufacture complex solvents, and the only chemical that may be made at scale is MEA, which is made from commodity chemicals ethylene oxide (via ethylene) and ammonia. Bara's analysis suggests that that more complex solvents, if manufactured, would promptly breach the world's top 50 commodity chemicals.[118]

One of the biggest challenges for green solvent development is the synthesis of the solvent. Manufacturing MEA is simple. It is made from gaseous reagents with no solvent.[119] The synthesis of MEA does produce by-products such as diethanolamine and triethanolamine, but these by-products have commercial value.[118] Thus, from a manufacturing standpoint, MEA is one of the greener solvents. More-complex amines have been studied in recent years, and continue to increase in complexity, which will require costly multistep synthesis routes generating substantial amounts of waste and unknown by-products. Further, the production viability of advanced solvents is not yet clear, because their chemical precursors are not yet scaled and there may not be markets for their by-products.[118] Lastly, all of these chemicals are expected to be synthesised from petrochemical precursors. Thus, there is a critical need for GC to facilitate the synthesis and scale-up of carbon capture solvents.

The principles of GC are straightforward on how to tackle this problem. We anticipate that raw material sourcing can be provided from either biological or renewable sources such as biomass, amino acids, or biological sources, rather than petrochemicals. Chemical synthons such as carbon backbones and alcohol moieties can be recovered from biomass, whereas amine functionalities can be recovered from natural sources like chitosan. We question whether chemical precursors can be sourced from more *avant-garde* sources such as municipal waste streams or industrial waste sources such as agricultural runoff (which contains amine-rich fertiliser). We also advocate solvent-free synthesis and avoiding VOCs during manufacturing as a means to reduce waste. Chemical synthesis should be designed such that any unavoidable by-products would be value-added products, providing economic drivers for their sale rather than disposal as organic waste. Lastly, the use of catalysts or enzymatic processes would make manufacturing more atom and energy efficient.

3.2. Lifetime of the solvents/biodegradation

Going the distance. One of the tenets of GC is to use reagents that are environmentally benign and that can biodegrade, creating a paradox of solvent durability. The contradiction is readily apparent, with the challenge of designing a solvent that shows reduced heat-stable salt formation, durability toward hydrolysis, heat, and oxidative degradation for thousands of cycles during operation, yet biodegrades by essentially the same degradation pathways after use. Because the solvent is costly, it needs to be durable, and chemical manufacturers are forced to introduce a mélange of chemical additives such as antifoaming agents, anti-aerosols, antioxidants, and anticorrosion agents to keep the OPEX and CAPEX of the solvent down. Thus, the challenge is, how do we prioritise the need for durability during use vs. biodegradation after being released? The easiest solution (pun intended) is to not make as much waste by minimising chemical degradations, or minimise fugitive emissions, though these are easier said than done.

We postulate whether a solvent kill-switch could be employed the moment the solvent or one of its degradation products is emitted from the CCUS infrastructure (Fig. 14). We envision the incorporation of chemical moieties that are thermally and oxidatively stable but unstable to external stimuli (*e.g.*, UV light) added to solvents, where exposure to natural light could begin the degradation process or denature them so that they are no longer toxic.

Fig. 14. In a perfect world, solvents would contain a solvent kill-switch to turn on biodegradation.

Another concept is the use of chemical chelators that complex with the unwanted and toxic material, chemically converting it into a biodegradable substance that could be disposed of with minimal harm to the environment. We take inspiration from natural gas sweetening, in which highly toxic H_2S (lethal at 4 ppm) can be made innocuous after chelation and reaction with iron chelates or triazine.[120] It remains likely that degradation products could be broken down selectively, as they will have distinctive functional groups (nitrosamine) that are not commonly found in nature. While not optimal, chemical chelats could be designed to complex and passivate degradation products at emission locations from the plant or in water tables surrounding the capture unit. We envision that extremophiles or other exotic bacteria, or fungi could be used in this process, assuming they might have (or be engineered to have) enzymes that could break down and chemically digest any of the degradation products.

3.3. Disposal/recycling to useful products

Circling the drain. Assuming the plant has reached its useful life span of 30 years and is decommissioning, the next challenge is what to do with the millions of litres of solvent in the unit. We cannot burn the spent material, because that is wasteful, creates emissions, and there are no places to store millions of litres of flammable solvent. In a perfect world, spent solvent could be reconstituted or used as a chemical synthon for value-added products or used as fertiliser, though to our knowledge, no studies yet exist. Ironically, we have yet to find the means to make enough solvent (*vide supra*), yet we should also be considering methods to deal with spent solvent. Thus, there is a critical need to decipher how spent solvent could be recycled or reconstituted into value-added products. This, of course, is highly dependent on the solvent in question. We do emphasise that GC can start looking at chemical motifs common to CO_2 capture solvents (*e.g.*, amines, alcohols) that could be harvested and used as chemical precursors or reagents for useful products. This has worked with SO_2 being converted to gypsum for cement board. Ideally, the amines could be made into a type of fertiliser, which would provide an environmental benefit, though any recycling or reconstitution would extend the life cycle of the solvent to not just be a "one and done."

4. Head #4. Transportation/storage

There are many reviews on storage and mineralisation, which by themselves are extensively studied and can justify a review on their own; thus, this perspective will briefly touch on alternative concepts that may be areas of focus for green chemists. CO_2 is generated at specific points of emissions, though utilisation (so far mainly enhanced oil recovery (EOR) and sequestration sites (mainly saline aquifers) are often thousands of miles away. How do we handle CO_2 to compress it, move it, and sequester it more efficiently? Head 4, is best tackled by finding innovative and regional storage options that minimize transportation.

As such, the transport of CO_2 requires costly and inefficient infrastructure and is emissive. For pipeline transportation (3100 km; 44.7 Gt of CO_2 worldwide) the average estimated construction cost in the US is about $20K to 30K per inch per km. In terms of OPEX, for a throughput of >10 million tons per year, transport cost can be less than US$1–10/ton of CO_2 per 100 km.[121] Several technologies can be envisaged, depending on the physical state under which CO_2 is transported (liquid, gaseous or dense phase). Gaseous CO_2 is typically compressed to a pressure above 8 MPa to increase its density, and thereby make it easier and less costly to transport (by minimising frictional losses and avoiding installation of booster stations).

The quality of CO_2 greatly matters: dry (moisture-free) CO_2 is not corrosive to the carbon-manganese steels customarily used for pipelines, even if the CO_2 contains contaminants such as oxygen, hydrogen sulphide, and sulphur or nitrogen oxides. Moisture-containing CO_2 is corrosive, and therefore should require a resistant (at least internally coated) alloy or a continuous polymer coating. A CO_2 pipeline crossing populated areas should be avoided, and quantitative risk analysis should be conducted, including maximum H_2S content tolerated, detailed route selection, pressure protection, leak detection and other design specifications.[122]

CO_2 can also be transported as a liquid in ship, road, or rail tankers that carry CO_2 in insulated tanks at a temperature well below ambient, and at much lower pressures. Safety and CO_2 quality requirements listed previously apply as well to those types of transportation.

Getting around. Can we move compressed CO_2 easier? Cheaper? To avoid again the stripping step, can we store CO_2 in a condensed liquid carrier and pump it, then compress the liquid, and then regenerate the solvent? This saves on mechanical compression since the compression is done on a liquid, not a gas. As mentioned earlier, disruptive stripping methods are progressively emerging, some of which could fit in such a scenario. Electrochemical stripping, like in the EMAR process developed by Hatton at MIT[45] where stripping at high pressure can be done at room temperature, may be envisaged. Still, there is, of course, the issue of the concentration of CO_2 in such rich phases that will potentially be transported. At 8 MPa and 25°C, CO_2 has a density of 765 kg/m^3, to be compared with 2,200 and 1,580 kg/m^3 for sodium and ammonium bicarbonate, respectively. CO_2-dense adducts that remain liquids at room temperature and high pressure can surely be found. The second objection is, of course, the safety: accidental release and explosive CO_2 blow-off is to be avoided. Many physical and chemical stimuli favouring capture or release have been reported (see Section 1) and for sure, some may conversely be used to temporarily, and on demand, freeze or block the stripping.

Fig. 15. CO_2 transportation: what is the most direct route to cut off the emissions? Graphics: Eulalia Claros in EPR 2015, PE 569.031

4.1. Storage/EOR use

Storage and the sustainability, safety and risks. As for transportation, CO_2 to be stored is handled in a compressed liquid phase. It is generally injected into saline aquifers in a perspective of carbonate formation under high pressure conditions. The issues of leakage and seismicity induction generally raise a strong concern among the populations, and many countries have excluded on-shore geological storage. How/where to safely mineralise CO_2 and store it? Are there different mineralisation reactions we can look at? Are there alternative storage sites or chemical complexing agents? Can we mineralise directly during capture (by mineral carbonation),[123] and on which substrates? As seashells do, can we promote precipitation of carbonates in sea water? With wastewater? Can we use solid waste material from the mining[124] or building[125] industries as substrates? Can mineral carbonation benefit from centuries of expertise in heterogeneous catalysis and be activated by soluble agents? As detailed in the next section, mineral carbonation simultaneously addresses many issues: it is capture and storage (as solid carbon) without stripping, compression, or seismicity issues. Yet, it is energy intensive for kinetic reasons (limiting mass transfer on solid-liquid-gas reactions). Can amine scrubbing chemistry mediate/catalyse mineral carbonation?[126] Can the injection of solid or liquid captured CO_2 be made practicable? This would require biocompatible organic (*e.g.*, amino acid carbamates) or inorganic (carbonates) adducts. How costly would that be?

Not In My Back Yard (NIMBY)! One of the biggest challenges for transportation is the challenge of building CO_2 pipeline infrastructure. The general public is often receptive to efforts to remove and sequester CO_2, though when it comes to building pipelines or sequestration, the challenge may be more than just the CAPEX of the infrastructure. The biggest challenge is public perception, because the public is reluctant to have such infrastructure anywhere close to where they reside. Thus, the most sensible and sustainable answer for Head # 4 may not be to erect CO_2 "highways," but rather to build smaller regional networks where, if possible, targeted short channels to direct sales and local markets could be used. Here, the transportation could be minimised, requiring less energy and infrastructure (Fig. 15). Building utilisation unit(s) next to the capture unit can be a reasonable method to pool CAPEX and OPEX. Conducting integrated capture and chemical utilisation by skipping stripping, compression, and transportation costs may, at the end of the day, be the most promising and sustainable/green option (see Head # 5).

5. Head #5. Utilisation

Now that we have CO_2 captured and condensed in solution, transported or not, can we use it as a commodity for chemical processes and products?

Warning: as for capture and storage, we assume that there should/will not be a unique universal solution. Capture and utilisation must be adapted to various cultural, geological, and industrial contexts throughout the globe, even within the same country. Therefore, the broadest possible portfolio of solutions should be developed to cover this diversity of situations, scales, and sources. Some tracks may be relevant for very small scales while others may tackle large ones.

CO_2 utilisation has at least two objectives. The first is to lead to end products and/or services meeting a substantial demand. In terms of economic model, the margins of production of these products must cover the cost of capture and transformation, and the residual benefit must exceed those being reached by competing pathways operating from fossil-based resources, if any. The second objective is to sequester CO_2 during a period of time that starts from the moment of capture up to the hypothetical degradation of the product back to CO_2. To be fully environmentally relevant, this latter criterion must take into account both the amount of CO_2 avoided during the entire capture to the utilisation chain of value (from cradle to grave) and the duration of CO_2 immobilisation into the corresponding commodity. A third aspect is the global environmental imprint of the capture and utilisation chain value, which encompasses the reduction of carbon dioxide emission and requires a thorough life-cycle assessment.[127]

This section will focus on processes that have been or may be coupled in series to capture OR integrated directly with capture; in other words, it deals with transformations that can potentially be conducted from flue gas or from the rich solutions. The idea is to look at what can be done with CO_2 rather than waste the stripping and compression energy and inject CO_2 underground. In fact, that investment is essentially buried with no value added. If we skip those steps, can't utilisation directly pay the price of capture/regeneration? Even a multidisciplinary army of experts cannot successfully address the five heads to convert the current substances into ones with viable chain value. Why not gather our forces into an all-in-one battle*, i.e.*, a one-pot CCUS process? CO_2 is the only carbon source feeding numerous plants, allowing them to elaborate not only fuels but monomers and smart platform molecules, drugs, and even material. Maybe yield and rates are low, but the approach is sustainable and there is room for improved biomimetism. For any given target molecule, the ideal scenario of CO_2-based production would involve carbon atoms coming mainly if not exclusively from CO_2, hydrogen from non-fossil sources (as opposed to the current situation; *i.e.*, electrons from renewable energies, protons from water) and heteroatoms from recycled waste material.

Two distinct subsections will detail by priority potential innovative utilisations of CO_2 as a reagent (Fig. 16a, b) or a reactant (Fig. 16c, d). In fact, CO_2 has found several utilisations related to its physical or biological properties, respectively, as an extracting (EOR and associated; Supercritical Fluid Chromatography), working, or heating/cooling fluid (Allam cycle, CO_2 lasers,) or as a commodity for plant growth and food production. These are technically utilisation, not transformation, each of which has a different associated sequestering duration. As the market for CO_2 is far smaller than the amount emitted, head 5 can best be tackled by identifying as many utilization pathways as possible.

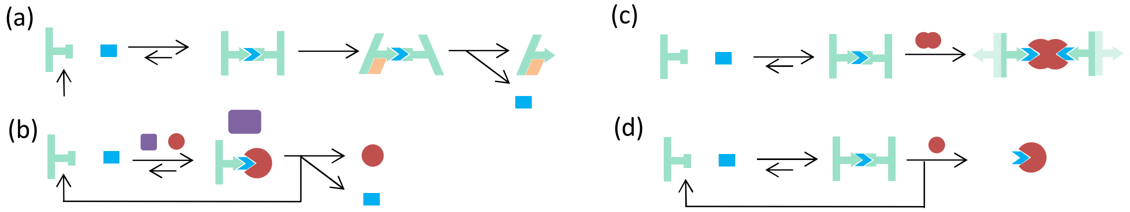

Fig. 16. Utilizing CO_2 as a reagent or as a reactant in integrated approaches. Nonexclusive paradigms of integrated CCUS: CO_2 as a temporary reactant without (a) or with capture agent recovery (b). CO_2 as a building block for the production of materials and feedstock without (c) and with capture agent recovery (d). Green : capture agent. Blue : CO2; orange : reactant for capture agent transformation; purple, pink : metal cations; red : co-nonomer for material formation; reactant for CO2 trnasformation.

5.1. CO_2 as a reagent

CO_2 capture converts blends of neutral capture agents into ion pairs or hydrogen bonded species. Although reversible, this coupling phenomenon inevitably alters the reactivity of the reactants (CO_2 and the capture agents) and provides adducts with new physical and chemical properties. In complement to trying to produce traditional intermediates or products, whose widespread use is related to their historical accessibility through industrial purification and conversion process from fossil resources, why don't we produce new (CO_2-based only) molecular systems with new properties?

5.1.1. Physical: Switchable polarity solvents and polymers. The majority of 3rd generation solvents may be recycled and utilized in a myriad of uses as switchable materials or simply as solvents themselves. Switchable materials are materials that can serve two purposes, whether as solvents that can switch between polarity, miscibility, or as functional materials that can perform multiple functions, minimizing waste, thus improving atom efficiency.[128] Water-lean solvents are in essence switchable polarity solvents (first identified by Jessop) as they are low-polarity molecular liquids that react with a chemical trigger gas, *i.e.* CO_2 to become polar ionic liquids.[53] Switchable materials have been identified for various applications ranging from water-purifications, recycling of plastics, phase change catalysis, polymers, liquid-liquid separations and reusable surfactants.[128] Water-lean solvents in their CO_2-rich solutions are strongly polar and protic, they can replace water or ionic liquids, while the lean forms are organic solvents of medium polarity.

5.1.2. Chemical: CO_2 as a thermolabile protecting/modulating group in synthetic chemistry. CO_2 can be used to modulate the reactivity of Lewis-base reacting species involved in multistep syntheses and requiring a preliminary protecting step (Fig. 16a). CO_2 may indeed be used as an agent delivering adducts that are less inert and robust than the tertbutoxycarbonyl (Boc) and fluoromethyloxyacrbonyl (Fmoc)-protected analogues. Yet, this masking reaction allows tuning of the reactivity or the rate of release of the free substrate to be further transformed. Either in the gaseous or supercritical form (a few catalytic processes carried out in scCO2 as the reaction solvent and temporary protecting group)[129] CO_2 has started to be used as a green auxiliary to favour the monoalkylation/acylation of amines[130, 131] or to modulate polymer curing, relying on diamines cross-linking.[132] Although the duration of sequestering is low (hours), CO_2 may advantageously replace toxic, highly impacting, or simply chemical agents produced from nonrenewable carbon resources. The favoured subsequent transformation of the capture agent may pay part or all of the energetic price for CO_2 stripping. This masking/protecting chemistry consisting in true capture may be conducted on flue gases and be applied to the manufacturing of industrial amines and to paint and polymer curing.

5.1.3. Coordination: capture adduct as metal ligands. Since adducts generated from CO_2 capture are frequently anionic, they can readily bind oxophilic metal centres.[133] When using binders that display multiples sites, such as polyamine, polycarbamates are obtained. These species are CO_2-sourced analogues of oxalates, succinates, EDTA, which are chelating or bridging partners, can be obtained. Therefore, these species can be valorised for metal extraction in sustainable hydrometallurgical processes (liquid-liquid[134]; liquid-solid[85]) in which thermal stripping can advantageously replace chemical stripping performed by concentrated acid/base, which generates high volumes of effluents (Fig. 16b). Given their composition and structure, the resulting CO_2-sourced organometallic complexes are synthetic analogues of RuBisCO (Ribulose-1,5-bisphosphate carboxylase/oxygenase), the famous enzyme performing CO_2 fixation through C-C coupling in the Calvin cycles.[135] In this gold-standard system, CO_2 is involved both in the coordination of the reactive metal centre and as a reactant to perform the C3 → C4 elongation of the substrate (see next section). It appears that virtually all metal cations and CO_2 capture adducts reported so far can be used as building blocks to be assembled into molecular complexes and/or metal-organic frameworks (Fig. 16c) with unprecedented physical and chemical properties.[136, 137]

As for alkaline earth carbonate, which results from CO_2 capture with the alkaline earth cations–water couple, integrated capture and self-assembly can, in principle, be conducted with flue gas. As with a vast majority of complexes and materials, the linkages within such architectures may be sensitive to hydrolysis, and in this very case, to heat. Hence, this approach delivers materials whose stability domain must be assessed and may be tuned by screening the building blocks used, the assembly conditions, and the potential post-processing. Conversely, it may deliver structures that can potentially be disassembled and whose constituents can/may be recycled and reassembled on demand. The design of materials and catalysts whose components can be replaced/recycled on demand upon specific stimuli certainly meets the current standards of sustainable development.

Although the volume and duration of CO_2 sequestering may be modest, the infinite scope of accessible structures and properties allows hope that we can produce architectures with unique properties and thereby provide temporary utilisations of CO_2 associated with high added values.

5.2. CO_2 as a reactant and building block toward fully CO_2-sourced chemicals and materials

The current architecture of the industrial assembly line yielding fine organic chemicals and polymers relies on a library of C1 to C4 aliphatic hydrocarbon building blocks and benzene derivatives. CO_2, which is a C1-as synthon or starting material, has so far mostly led to C1 products (carbon monoxide, carbonates, formic acid/formates, methanol, methane, urea, dimethylcarbonate). When used as a carbonyl source to form higher adducts, it is generally reacted by covalent connection to one or two nucleophilic heteroatoms or to an acid-base Lewis pair, a scheme that is reminiscent of the capture process. Apart from the synthesis of salicylic acid, CO_2 is still rarely used for C-C coupling and remains a "+1 chemical partner" in the sense that it is rarely coupled to itself for carbon chain elongation leading to organic platform molecules, whose backbones are mainly or entirely sourced from CO_2.

Challenges in CO_2 utilisation as a reactant reside in integrating these transformations with capture (to deliver an economically viable capture and transformation value chain) in mild conditions with catalysts involving low cost or metals recycled from waste (*i.e.*, associated with low energy requirement and imprints). Another challenge is to expand upon the degree of incorporation of CO_2 from being simply a C1 reagent to higher carbon content products with incorporation of as many CO_2s as possible. Here, we envision developed industrial production lines of organic feedstocks mainly sourced from CO_2, including but not limited to short hydrocarbons, olefins, nanotubes, graphene, *etc*.

5.2.1. C1 (single carbon) products by integrated/sustainable CCUS. Apart from the conversion into carbonates, CO_2 transformation into C1 products is inevitably a thermodynamically uphill journey that requires high energy species—at least electrons and frequently protons. One of the privileged targets for CO_2 transformation is CO: many important organic chemicals can be produced from the CO and H_2 mixture known as syngas. CO can industrially be produced from CO_2 and CH_4 by a two-step process called autothermal reforming. This transformation and the chemical nature of syngas immediately raise the issue of the sources of H_2 and CH_4, which are still mainly fossil-based. In terms of kinetics, the use of nonthermal plasma activation allows CO_2 hydrogenation at standard temperature and pressure and was recently validated for the direct capture and transformation into CO[138] and into methanol.[139] We note that when accounting for all reagents, H_2 is not free and that it is more favourable to utilize H_2 directly than make into carbon-based fuels. We advocate that until large scale H_2 storage or battery technologies become more prominent for energy storage, it is at least desirable to store stranded renewable energy in the form of a carbon-based fuel than dumping the excess electrons as heat.

Recent developments in heterogeneous and homogeneous catalysis have shown that this fertile field may soon allow one to browse the whole portfolio of C1 molecules that can be envisaged from CO_2, while operating in capture-like conditions. In fact, catalysis can now be performed on anionic carboxylates at atmospheric pressures, replacing physically dissolved CO_2 for CO_2 captured at high concentrations in an ionic medium.[140] With these new reactive pathways, new methodologies for tandem amine-based capture and conversion into conventional targets such as CO, methanol, and formate are being reported.[141-144] There is a potentially infinite spectrum of new reactive pathways that can be designed for using CO_2 as a methylation agent or alternative C1 synthon directly from flue gas or capture adducts. As mentioned earlier, to avoid simply shifting the problem, attention must be drawn to the sources of protons and electrons used. In this perspective, electroreduction[145] or photosynthetically inspired pathways such as visible-light photoreduction in an aqueous medium[146] represent some of the grails of sustainable CO_2 utilisation. Many challenges herein remain to be addressed, including the identification of the factors governing the selectivities, the improvements of the rates, energy efficiency, and stability, which currently preclude any development, and the use of low cost/recycled metals or even organocatalysts.

Most of these C1 products, which will find use as fuel or fertiliser, are estimated to have an average CO_2 sequestering potential of 6 months.[147]

5.2.2. Mineral carbonates. This transformation is the only downhill route from a thermodynamic point of view. Mineral carbonation consists of the exothermal conversion of minerals (mostly calcium or magnesium silicates) with CO_2 into inert carbonates (Fig. 16c). The current bottleneck resides in the unfavourable kinetics of this triphasic reaction, which requires heat, pressure, and chemical and/or mechanical activation to reach an acceptable productivity. This is again where experts in catalysis are needed. Interestingly, amines used in capture were reported to efficiently catalyse some of the multiple steps involved in this process, which could open the way toward integrated capture and utilisation from flue gases.[126, 148]

In situ mineral carbonation is a potential strategy for CO_2 storage of very large capacity. (The calcium and magnesium carbonate mineral rock deposits on Earth are theoretically sufficient to fix all the CO_2 that could be produced by the combustion of all available fossil fuel reserves.[149] This combines the advantages of being one of the only permanent, leak-free, fixation methods with no need for long-term monitoring. Recently, a large-scale demo of sequestration was attempted where CO_2 was injected in wells in Iceland containing basaltic lavas and hyaloclastites at depths 400-800 m.[150] Surprisingly, the majority of the CO_2 was found to be mineralized in less than 2 years.[150] Studies like this suggest that permanent sequestration may be feasible on reasonable time scales.

In situ mineral carbonation is not only a storage but also a utilisation strategy: waste materials like steel-converter slag, fly ash or mine tailings can be transformed into "valuable" calcium or magnesium carbonates, products which are currently meeting the construction market as slurry for green cement manufacturing (Fig. 17). While the solidity of the associated economic model and the maturity of the technology are witnessed by the many start-up companies emerging in the field (CarbonCure (Canada), Mineral Carbonation International (Australia), De Beers (South Africa), Cambridge Carbon capture (UK)), there is still plenty of room for green chemists to reduce the energy and water demand for this process, by using waste/untreated water, low-quality heat and co-producing silica.

Fig. 17. Green cement from waste material. http://blog.drupa.com/en/3d-printing-green-cement-made-from-industrial-waste-2/

5.2.3. From organic monomers to organic polymers

At present, CO_2 remains a C1 synthon and one of its most useful applications consists in replacing the extremely toxic reagent phosgene in organic coupling with Lewis bases (mainly amine and alcohol derivatives) to produce carbamates and carbonates.[151]

CO_2 as a plus-one molecule. Through what can be formally viewed as capture and *in situ* irreversible conversion, CO_2 was reported so far to yield molecular carbamates,[152] guanidines,[153] formamides,[153] and oxazolidones.[154, 155] As in the industrial synthesis of urea, the energy released by the first exothermal (capture) step is used to thermodynamically favour the subsequent endothermal step instead of being dissipated as heat. During such a sequence, the capture agent is sacrificed, as it contributes to the backbone of the end product. This raises again the question of the scale of applicability and of the sourcing of the capture agent. The same applies for the polymeric counterparts of some of these monomeric products. The one-pot capture and polymerisation approach was validated several decades ago for the synthesis of polycarbonates and polyurethanes,[156] which represent significant shares in the global consumption of organic polymers (respectively the second and fifth sales values with 4.3 and 1.4 Gtons produced in 2015). In addition to avoiding safety issues, replacing phosgene with CO_2 reduces by up to 20% the carbon footprint and the global environmental footprint associated to the fabrication of these materials,[157] which can incorporate up to 40% CO_2 by mass. Production plants with annual capacities of thousands of metric tons are being started with plans to use materials that incorporate CO_2 in mattress manufacturing (https://www.co2-dreams.covestro.com/). Yet, blending with petrochemical-derived co-monomers is often required to improve the mechanical properties; alternative co-monomer production pathways starting from CO_2 would clearly be beneficial.

From these promising examples, we ask whether, inspired by performing industrial synthesis of salicylic acid with CO_2, its +1 role can be extended to the production of strategic organic monomers by C-C coupling, such as benzoic acid from benzene, acetic acid from methane, acrylic acid from ethylene (to replace the current production by aerobic oxidation of propylene).[158] With these entry points, and once efficient pathways for sustainable hydrogenation/electroreduction have been established, hydrocarbon and olefin homologation can be envisaged through carbonylation-reduction tandem reactions. With the set of C2-C4 monomers in hand, current key organic polymers (polystyrene, polyethylene, and polypropylene) can be partly or entirely sourced from CO_2 (Fig. 18). Beyond these conventional materials historically developed from petrochemical sources, new organic (light, robust) materials with unprecedented properties can be obtained from this greenhouse gas or from renewables. Behind this question is the question of monomer synthesis from CO_2 (*vide infra*).

Fig. 18. Plastic from CO_2: a Novomer process (https://www.chemistryworld.com/news/recycling-co2-to-make-plastic/3003416.article)

5.2.4. CO_2 as a real monomer for carbon copy. While hitherto unstable molecular silicon dioxide was recently isolated by chemists for subsequent controlled oligomerisation,[159] we ask whether carbon dioxide can conversely be polymerised or at least oligomerised. When comparing successful reactive pathways delivering C_n ($n > 1$) vs. C1 building blocks, there clearly is a substantial gap in number and degree of maturity. We herein focus in priority on the CO_2-only approaches to deliver these commodities of higher numbers of carbon atoms (Fig. 19), where again, catalysis, electrocatalysis, and photocatalysis will be the key players.

In the C2 series, oxalate is *a priori* the most obvious species that can be obtained by dimerisation of the radical resulting from monoelectronic (electrocatalytic) reduction of CO_2.[160] Oxalate is the entry point to monoethylene glycol, glycolic and glyoxylic acid, acetic ethanol and ethylene, ethylene being a key monomer for the production of PET (polyethylene terepthalate, Fig. 18), which is currently targeted by a joint venture between Coca-Cola and Liquid Light (acquired by Avantium).

Looking again at what nature has succeeded in developing through millennia of Darwinian selection and evolution, Moran has recently[161] managed to mimic the acetyl-CoA pathway of CO_2 fixation (one of the six known to date), in which native metals provide electrons to reduce CO_2 into acetate and pyruvate (with protons coming from water). Can the five other natural pathways be mimicked, simplified, and developed by chemical or biochemical approaches (see next paragraph) together with totally new artificial ones? Can they operate at standard temperature and pressure, and reach acceptable levels of productivity for industrial development?

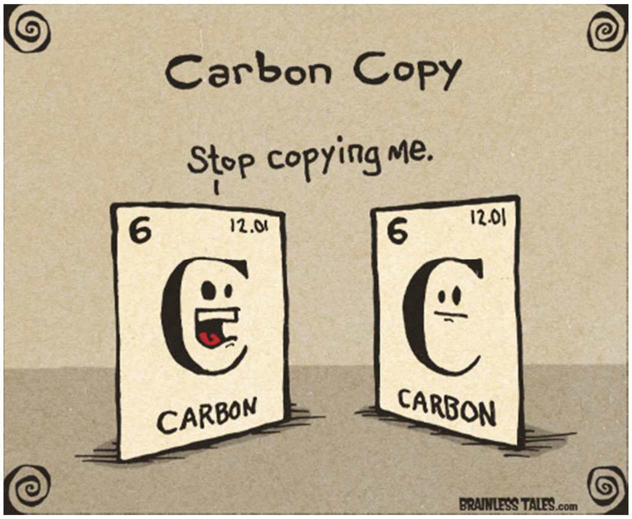

Fig. 19. Carbon copy: oligomerisation of CO_2-reduced species. http://www.brainlesstales.com/2013-04-15/carbon-copy

Beyond C1 products, (photo)electrochemists are also starting to report catalytic systems (copper-based, mainly[162]) yielding as major C2 adducts ethanol and ethylene,[163] which are the workhorses of petrochemical companies. The number of electron transfer steps and intermediates is growing exponentially with the number of carbon atoms to be linked within the chain to be produced, yielding complex mixtures. The lack of selectivity of these catalytic processes is often perceived as a barely surmountable challenge, which may prevent any future upscaling and technology transfer.

If effort shall remain focused on energy efficiency and resource management, we suggest again to envisage the design of multidisciplinary integrated processes to overcome this issue of selectivity and propose innovative solutions. From a historical and industrial point of view, such mixtures are crude CO_2-based oil, which may be processed by mature refining technologies. Therefore, tandem conversion or conversion/purification approaches should be explored with priority. This suggestion is inspired by recent breakthroughs reporting that coupled chemical (bio)catalytic transformations allowed to sequentially perform CO_2 activation into C1 intermediates followed by *in situ* coupling into C2-C4 olefins[164, 165] or alcohols.[166] In fact, these emerging multistep cascades are the embryonic analogues of the metabolic cycles designed by nature to produce the organic molecules of life from CO_2. The fields of possibility in the design of new man-made cycles is almost infinite, ranging from fully biochemical, such as the artificial Calvin-like cycle,[167] to purely chemical, with the production of C4–C8 Gasoline from CO_2 and H_2 through iron-based catalysis.[168]

On the way to produce crude oil from CO_2, one challenge remains fully open and to be addressed by these new “chemobolic” cycles: the production of benzene rings from CO_2. So far, triazine is the only aromatic adduct whose conjugated backbone is produced from CO_2 though the trimerisation of CO_2-based urea. Yet, pure carbon-based materials, such as the nanofibers widely used in automotive and aviation construction[169] and multiwalled nanotubes used for water filtration systems, or as constituents to produce conducting polymers and battery electrodes, recently proved to be accessible from CO_2.[170] Remarkably, these recent reports illustrate how fertile the integrative system engineering approach can be, opening the way toward either concomitant valorisation/recycling of metal-slags or renewable energy storage (Fig. 20).[171] If none of these innovative CCUS pathways was so far attempted directly from flue gas or capture adducts, which remains a necessity to design an economically viable CCUS value chain, there is no doubt that this challenge will soon be addressed by similar multidisciplinary and integrated approaches.

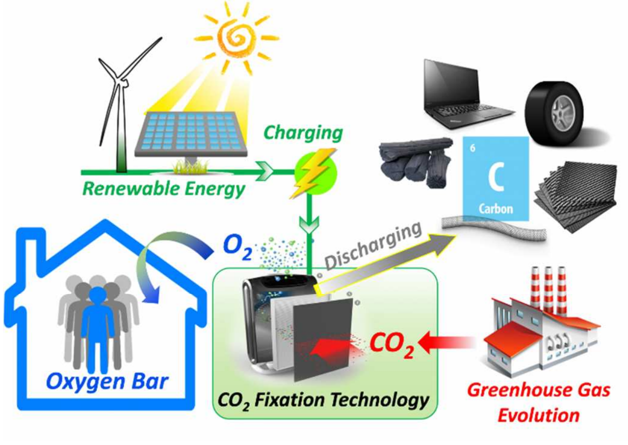

Fig. 20. A battery-inspired strategy for carbon fixation. https://phys.org/news/2017-08-battery-inspired-strategy-carbon-fixation.html

Conclusions

Herein we issued an academic and technological “call to arms” for GC and green engineering to address the complexity and the magnitude of CCUS. We presented CCUS as a five-headed hydra with many complexities and challenges that need to collectively be addressed to make CCUS a reality. Armed with the principles of GC and engineering, we emphasise that CCUS is not an unsolvable problem; rather, the problem is a mélange of energy, infrastructure, environmental impact, and time that must be considered equally. In this perspective, we highlighted challenges for all aspects of CCUS, identifying what has or has not been attempted, while also identifying swatches of white space and potential avant-garde concepts in hopes of fostering innovation or at least stoke conversation on the needs and focus areas to address this challenge.

We ask the research community to take heed and take up arms. We encourage the community to reach out to colleagues in adjacent fields to build synergistic programmes and efforts that can tackle the magnitude and complexity of this challenge. GC has made many processes and chemicals greener while providing some semblance of an economic driver; there remains no reason why this cannot be the case with CCUS. If we all take up arms and work together then there is no limit to the powers of GC to address any current or future challenges that humanity may face.

Thank you for your audience and we hope that you may join us on this journey. Sincerely, Julien Leclaire and David J. Heldebrant.

Acknowledgements

DJH would like to acknowledge the United States Department of Energy's (DOE's) Office of Science, Basic Energy Sciences, Early Career Research Program FWP 67038 for funding. Pacific Northwest National Laboratory is proudly operated by Battelle for the U. S. DOE. JL would like to acknowledge the French Agency for the Environment and Energy Management (ADEME) and the LABEX iMUST (ANR-10-LABX-0064) of Université de Lyon within the program "Investissements d'Avenir" (ANR-11-IDEX-0007) operated by the French National Research Agency (ANR) for funding.

Notes and references

1. P. T. Anastas, Warner, J. C. , *Green Chemistry: Theory and Practice*, Oxford University Press, New York, 1998.
2. P. T. Anastas and J. B. Zimmerman, *Env. Sci. and Tech.*, 2003, **37**, 94A-101A.
3. David S. Sholl and R. P. Lively, *Nature* 2016, **532**, 435–437.
4. GCP, Global Carbon Budget 2016, , http://www.globalcarbonproject.org/carbonbudget/16/files/GCP_CarbonBudget_2016.pdf).
5. *Journal*, 2014.
6. COP21 Paris Agreement, , http://ec.europa.eu/clima/policies/international/negotiations/paris/index_en.htm).
7. M. Bui, C. S. Adjiman, A. Bardow, E. J. Anthony, A. Boston, S. Brown, P. S. Fennell, S. Fuss, A. Galindo, L. A. Hackett, J. P. Hallett, H. J. Herzog, G. Jackson, J. Kemper, S. Krevor, G. C. Maitland, M. Matuszewski, I. S. Metcalfe, C. Petit, G. Puxty, J. Reimer, D. M. Reiner, E. S. Rubin, S. A. Scott, N. Shah, B. Smit, J. P. M. Trusler, P. Webley, J. Wilcox and N. M. Dowell, *Energy Environ. Sci.*, 2018, **11**, 1062—1176.
8. S. Zhao, P. H.M.Feron, L. Deng, E. Favre, E. Chobanon, S. Yan, J. Hou, V. Chen and H. Qi, *Journal of Membrane Science*, 2016, **511**, 180-206.
9. S.-Y. Lee and S.-J. Park, *Journal of Industrial and Engineering Chemistry* 2015, **23**, 1-11.
10. D. W. Keith, G. Holmes, D. S. Angelo and K. Heidel, *Joule*, 2018, DOI: https://doi.org/10.1016/j.joule.2018.05.006.
11. N. E. T. Laboratory, *Journal*, July 6, 2016, **1**.
12. https://www.power-technology.com/projects/taichung/).
13. *US Pat.,* U.S. Patent 1,783,901, 1930.
14. A.Singhand and K. S.´ephenne, *Energy Procedia*, 2014, **63**, 1678–1685.
15. Y.-J. Lin, E. Chen and G. T. Rochelle, *Faraday Discuss.*, 2016, **192**, 37-58.
16. P. M. Mathias, *Fluid Phase Equilib.*, 2014, **362**, 102-107.
17. P. M. Mathias, S. Reddy, A. Smith and K. Afshar, *Int. J. Greenh. Gas Control*, 2013, **19**, 262-270.
18. D. H. Van Wagener, A. Gupta, G. T. Rochelle and S. L. Bryant, *Oil Gas Sci. Technol. – Rev. IFP Energies nouvelles*, 2014, **69**, 1105-1119.
19. T. Madan, D. H. Van Wagener, E. Chen and G. T. Rochelle, *Energy Procedia*, 2013, **37**, 386-399.
20. M. S. Walters, R. H. Dunia, T. F. Edgar and G. T. Rochelle, *Energy Procedia*, 2013, **37**, 2133-2144.
21. S. Seo, L. D. Simoni, M. Ma, M. A. DeSilva, Y. Huang, M. A. Stadtherr and J. F. Brennecke, *Energy Fuels*, 2014, **28**, 5968-5977.
22. J. Septavaux, G. Germain and J. Leclaire, *Acc. Chem. Res.* , 2017, **50**, 1692-1701.
23. E. Grunwald and C. Steel, *J. Am. Chem. Soc.*, 1995, **117**, 5687–5692.
24. E. A. v. Nierop, S. Hormoz, K. Z. House and M. J. Aziz, *Energy Procedia*, 2011, 1783–1790.
25. P. M. Mathias, K. Afshar, F. Zheng, M. D. Bearden, C. J. Freeman, T. Andrea, P. K. Koech, I. Kutnyakov, A. Zwoster, A. R. Smith, P. G. Jessop, O. G. Nik and D. J. Heldebrant, *Energy Environ. Sci.*, 2013, **6**, 2233-2242.
26. R. J. Perry, B. R. Wood, S. Genovese, M. J. O'Brien, T. Westendorf, M. L. Meketa, R. Farnum, J. McDermott, I. Sultanova, T. M. Perry, R.-K. Vipperla, L. A. Wichmann, R. M. Enick, L. Hong and D. Tapriyal, *Energy Fuels*, 2012, **26**, 2528-2538.
27. T. Zhao, B. Guo, Q. Li, F. Sha, F. Zhang and J. Zhang, *Energy Fuels*, 2016, **30**, 6555-6560.
28. X. Wang, N. G. Akhmedov, D. Hopkinson, J. Hoffman, Y. Duan, A. Egbebi, K. Resnik and B. Li, *Appl. Energy*, 2016, **161**, 41-47.
29. D. Malhotra, J. P. Page, M. E. Bowden, A. Karkamkar, D. J. Heldebrant, V.-A. Glezakou, R. Rousseau and P. K. Koech, *Ind. Eng. Chem. Res.*, 2017, **56**, 7534-7540.
30. P. Broutin, P. Briot, S. Ehlers and A. Kather, *Energy Procedia*, 2017, **114**, 2561–2572.
31. D. J. Heldebrant, P. K. Koech, V.-A. Glezakou, R. Rousseau, D. Malhotra and D. C. Cantu, *Chem. Rev.* , 2017, **117**, 9594–9624.
32. L. M. Rossi, N. J. S. Costa, F. P. Silvaa and R. Wojcieszaka, *Green Chem.*, 2014, **16**, 2906-2933.

33. A. Mukhopadhyay, R. Ganguly, S. Sen and I. K. Puri, *International Journal of Heat and Mass Transfer*, 2005, **48**, 3485-3492.
34. A. Behr, G. Henze and R. Schomäcker, *Adv. Synth. Catal.*, 2006, **348**, 1485-1495.
35. F. Zheng, D. J. Heldebrant, P. M. Mathias, P. Koech, M. Bhakta, C. J. Freeman, M. D. Bearden and A. Zwoster, *Energy Fuels* 2016, **30**, 1192-1203.
36. A. S. Joel, M. Wang, C. Ramshaw and E. Oko, *International Journal of Greenhouse Gas Control*, 2014, **21**, 91-100.
37. S. Wu, L. Zhang, B. Sun, H. Zou, X. Zeng, Y. Luo, Q. Li and J. Chen, *Energy Fuels*, 2017, **31**, 14053–14059.
38. A. Alabdulkarema, Y. Hwang and R. Radermacher, *Applied Energy* 2015, **147**, 258-268.
39. S. J. Higgins and Y. A. Liu, *Ind. Eng. Chem. Res.*, 2015, **54**, 2526−2553.
40. T. Chronopoulosa, Y. Fernandez-Diez, M. M. Maroto-Valer, R. Ocone and D. A. Reay, *Microporous and Mesoporous Materials*, 2014, **197**, 288-290.
41. S. J.McGurk, C. F.Martín, S. Brandani, M. B.Sweatman and X. Fan, *Applied Energy*, 2017, **192**, 126-133.
42. H. Nigar, B. Garcia-Baños, F. L. Peñaranda-Foix, J. M. Catalá-Civera, R. Mallada and J. Santamaría, *AIChE Journal*, 2015, **62**, 547-555.
43. J. Yang, H. Y. Tan, Q. X. Low, B. P. Binks and J. M. Chin, *J. Mater. Chem. A*, 2015, **3**, 6440-6446.
44. J. Wilcox, R. Haghpanah, E. C. Rupp, J. He and K. Lee, *Annu. Rev. Chem. Biomol. Eng.* , 2014, **5**, 479–505.
45. M. C. Stern, F. Simeon, H. Herzog and T. A. Hatton, *Energy Environ. Sci.*, 2013, **6**, 2505-2517.
46. D. Nguyen, J. Stolaroff and A. Esser-Kahn, *ACS Appl. Mater. Interfaces*, 2015, **7**, 25851−25856.
47. K. Tanaka, T. Fujiwara, H. Okawa, T. Kato and K. Sugawara, *Jpn. J. Appl. Phys.*, 2014, **53**, 07KE14.
48. O. Y. Orhan, Y. K. Hulya, Y. Ersan and E. Alper, *Energy Procedia*, 2017, **114**, 66-71.
49. J. Mancebo, D. Isabey, H. Lorino, F. Lofaso, F. Lemaire and L. Brochard, *Eur Respir J.* , 1995, **11**, 1901-1909.
50. C. A. Hunter and H. L. Anderson, *Angew. Chem. Int. Ed.*, 2009, **48**, 7488-7499.
51. R. Steinhardt, S. C. Hiew, H. Mohapatra, D. Nguyen, Z. Oh, R. Truong and A. Esser-Kahn, *ACS Cent. Sci.*, 2017, **3**, 1271-1275.
52. D. M. Rudkevich and H. Xu, *Chem. Commun.*, 2005, **0**, 2651-2659.
53. P. G. Jessop, D. J. Heldebrant, X. W. Li, C. A. Eckert and C. L. Liotta, *Nature*, 2005, **436**, 1102-1102.
54. C. M. Mömming, E. Otten, G. Kehr, R. Fröhlich, S. Grimme, D. W. Stephan and G. Erker, *Angew. Chem. Int. Ed.*, 2009, **48**, 6643-6646.
55. D. W. Stephan, *Acc. Chem. Res.*, 2015, **48**, 306-316.
56. DominikNiedek, J. P. Wagner and P. R.Schreiner, *Journal of Analytical and Applied Pyrolysis*, 2017, **124**, 439-445.
57. P. K. Koech, J. Zhang, I. V. Kutnyakov, L. Cosimbescu, S.-J. Lee, M. E. Bowden, T. D. Smurthwaite and D. J. Heldebrant, *R. Soc. Chem. Adv.*, 2013, **3**, 566-572.
58. G. A. Whyatt, A. Zwoster, F. Zheng, R. J. Perry, B. R. Wood, I. Spiry, C. J. Freeman and D. J. Heldebrant, *Ind. Eng. Chem. Res.*, 2017, **56**, 4830−4836.
59. D. C. Cantu, J. Lee, M.-S. Lee, D. J. Heldebrant, P. K. Koech, C. J. Freeman, R. Rousseau and V.-A. Glezakou, *J. Phys. Chem. Lett.*, 2016, **7**, 1646-1652.
60. L. Liu, B. Lukose and B. Ensing, *ACS Catal.*, 2018, **8**, 3376-3381.
61. Y. Huang, G. Cui, Y. Zhao, H. Wang, Z. Li, S. Dai and J. Wang, *Angew. Chem. Int. Ed.*, 2017, **56**, 13293-13297.
62. *J. Org. Chem.*, 2018, **83**, 5138-5148.
63. P. V. Kortunov, L. S. Baugh and M. Siskin, *Energy Fuels*, 2015, **29**, 5990-6007.
64. P. V. Kortunov, L. S. Baugh, M. Siskin and D. C. Calabro, *Energy Fuels*, 2015, **29**, 5967–5989.
65. Pankaj Sharma, S. D. Park, I. H. Baek, K. T. Park, Y. I. Yoon and S. K. Jeong, *Journal*, 2012, **100**, 55-62.
66. M. I. Childers, J. M. Longo, N. J. V. Zee, A. M. LaPointe and G. W. Coates, *Chem. Rev.*, 2014, **114**, 8129-8152.
67. M. H. Chisholm, D. Navarro-Llobet and Z. Zhou, *Macromolecules*, 2002, **35**, 6494–6504.
68. Z. Qin, C. M. Thomas, S. Lee and G. W. Coates, *Angew. Chem. Int. Ed.*, 2003, **42**, 5484-5487.
69. D. J. Darensbourg, *Chem. Rev.*, 2007, **107**, 2388-2410.
70. D. J. Darensbourg, *Inorg. Chem.*, 2010, **49**, 10765-10780.
71. D. J. Darensbourg, R. M. Mackiewicz, A. L. Phelps and D. R. Billodeaux, *Acc. Chem. Res.*, 2004, **37**, 836-844.
72. M.Tomaszewska and A.Mientka, *Desalination* 2009, **240**, 244-250.
73. P. D.M., in *First Steps in the Origin of Life in the Universe*, ed. O. T. Chela-Flores J., Raulin F. (eds), Springer, Dordrecht, 2001.
74. C. M. Cavanaugh, S. L. Gardiner, M. L. Jones, H. W. Jannasch and J. B. Waterbury, *Science*, 1981, **213**, 340-342.
75. HorstFelbeck and G. N.Somero, *Trends in Biochemical Sciences*, 1982, **7**, 201-204.
76. P. M. Mathias, F. Zheng, D. J. Heldebrant, A. Zwoster, G. Whyatt, C. M. Freeman, M. D. Bearden and P. Koech, *ChemSusChem*, 2015, **8**, 3617-3625.
77. O. Alvizo, L. J. Nguyen, C. K. Savile, J. A. Bresson, S. L. Lakhapatri, E. O. P. Solis, R. J. Fox, J. M. Broering, M. R. Benoit, S. A. Zimmerman, S. J. Novick, J. Liang and J. J. Lalonde, *81. PNAS*, 2014, **111**, 16436-16441.
78. P. Mirjafari, K. Asghari and N. Mahinpey, *Ind. Eng. Chem. Res.*, 2007, **46**, 921–926.
79. Y. J. Choi, D. Sivanesan, J. Lee, M. H. Youn, K. T. Park, H. J. Kim, A. N. Grace, I. H. Kim and S. K. Jeong, *Journal of Industrial and Engineering Chemistry* 2016, **34**, 76-83.
80. C. A. Lippert, K. Liu, M. Sarma, S. R. Parkin, J. E. Remias, C. M. Brandewie, S. A. Odom and K. Liu, *Catal. Sci. Technol.*, 2014, **4**, 3620-3625.
81. P. G. Jessop and B. Subramaniam, *Chemical Rev.* , 2007, **107**, 2666-2694.
82. P. Pollet, R. J. Hart, C. A. Eckert and C. L. Liotta, *Acc. Chem. Res.*, 2010, **43**, 1237–1245.
83. Z. Lei, C. Dai and B. Chen, *Chem. Rev.*, 2014, **114**, 1289–1326.
84. M. Karimi, M. Hillestad and H. F. Svendsen, *Chem. Eng. Res. Des.*, 2011, **89**, 1229-1236.
85. G. Poisson, G. Germain, J. Septavaux and J. Leclaire, *Green Chem.* , 2016, **18**, 6436–6444.
86. *Germany Pat.,* US 8523979B2, 2013.
87. A. Arce, N. M. Dowel, N. Shah and L. F. Vega, *International Journal of Greenhouse Gas Control*, 2012, **11**, 236–250.
88. C. L. Davidson, D. J. Heldebrant, M. D. Bearden, J. A. Horner and C. J. Freeman, *Energy Procedia*, **114**, 6448-6454

89. J. J. Moore, A. Lerche, H. Delgado, T. Allison and J. Pacheco, *Proceedings of the Fortieth Turbomachinery Symposium*, 2011, DOI: https://doi.org/10.21423/R1S65C, 107-120.
90. PengPei, K. Barse, A. J.Gil and J. Nasah, *Int. J. Greenh. Gas Control*, 2014, **30**, 86-96.
91. A. Witkowski, A. Rusin, M. Majkut, S. Rulik and K. Stolecka, *Energy Convers. Manage.*, 2013, **76**, 665-673.
92. D. H. V. Wagener, Doctor of Philosophy PhD, The University of Texas at Austin, 2011.
93. A. Cousins, P. T. Nielsen, S. Huang, R. Rowland, B. Edwards, A. Cottrell, E. Chen, G. T. Rochelle and P. H. M. Feron, *Int. J. Greenhouse Gas Control*, 2015, **37**, 256–263.
94. N. Dai, A. D. Shah, L. H. Hu, M. J. Plewa, B. McKague and W. A. Mitch, *Environ. Sci. Technol.*, 2012, **46**, 9793–9801.
95. J. G. Thompson, R. Frimpong, J. E. Remias, J. K. Neathery and K. Liu, *Aerosol and Air Quality Research*, 2014, **14**, 550–558.
96. R. Haws, *In:Gas Processors Association Regional Meeting, Houston.*, 2001.
97. D. J. Heldebrant, P. K. Koech and C. R. Yonker, *Energy Environ. Sci.*, 2010, **3**, 111-113.
98. D. J. Heldebrant, C. R. Yonker, P. G. Jessop and L. Phan, *Chem. Eur. J.*, 2009, **15**, 7619-7627.
99. D. Yang, M. Hou, H. Ning, J. Zhang, J. Ma and B. Han, *Phys. Chem. Chem. Phys.*, 2013, **15**, 18123-18127.
100. H. J. Lee, K. I. Lee, M. Kim, Y. W. Suh, H. S. Kim and H. Lee, *ACS Sustainable Chem. Eng.*, 2016, **4**, 2012-2019.
101. M. S. Shannon, A. C. Irvin, H. Liu, J. D. Moon, M. S. Hindman, C. H. Turner and J. E. Bara, *Ind. Eng. Chem. Res.*, 2015, **54**, 462-471.
102. C. Wang, G. Cui, X. Luo, Y. Xu, H. Li and S. Dai, *J. Am. Chem. Soc.*, 2011, **133**, 11916-11919.
103. J. Wang, S. Zeng, L. Bai, H. Gao, X. Zhang and S. Zhang, *Ind. Eng. Chem. Res.*, 2014, **53**, 16832–16839
104. Y. Jiang, X. Liu and D. Deng, *107. J. Chem. Eng. Data*, 2018, **63**, 259–268.
105. *USA Pat.,* 2014.
106. T. Femmer, A. J.C.Kuehne and M. Wessling, *Chem. Eng. Journal.*, 2015, **273**, 438-445.
107. M. Kleiman, K. S. Brubaker, D. T. Nguyen and A. P. Esser-Kahn, *Chem. Mater.*, 2015, **27**, 4871−4876.
108. M. Nainar and A. Veawab, *Ind. Eng. Chem. Res.*, 2009, **48**, 9299-9306.
109. ECI Symposium Series, http://dc.engconfintl.org/co2_summit2/11).
110. E. J. Maginn, Ionic Liquids: Breakthrough Absorption Technology for Post-Combustion CO2 Capture. , https://digital.library.unt.edu/ark:/67531/metadc844696/).
111. G. S. Goff and G. T. Rochelle, *Ind. Eng. Chem. Res.*, 2006, **45**, 2513–2521.
112. C. Gouedard, D. Picq, F. Launay and P.-L.Carrettea, *Int. J. Greenh. Gas Control*, 2012, **10**, 244-270.
113. A. J.Sexton and G. T. Rochelle, *Int. J. Greenh. Gas Control*, 2009, **3**, 704-711.
114. G. Léonard, A. Voice, D. Toye and G. Heyen, *117. Ind. Eng. Chem. Res.*, 2014, **53**, 18121–18129.
115. A. M. Brandon, S.-H. Gao, R. Tian, D. Ning, S.-S. Yang, J. Zhou, W.-M. Wu and C. S. Criddle, *Environ. Sci. Technol.*, 2018, **52**, 6526-6533.
116. J. Yang, Y. Yang, W.-M. Wu, J. Zhao and L. Jiang, *118. Environ. Sci. Technol.*, 2014, **48**, 13776–13784
117. L. W. Diamond and N. N.Akinfiev, *Fluid Phase Equilibria*, 2003, **208**, 265-290.
118. J. E. Bara, *Greenhouse Gas Sci Technol.*, 2012, **2**, 162-171.
119. P. J. Chenier, *Survey of Industrial Chemistry*, Kluwer Academic/Plenum Publishers, New York, NY, USA 3edn., 2002.
120. M. K. Amosa, I. A. Mohammed and S. A. Yaro, *NAFTA*, 2010, **61**, 85-92.
121. S. Santos, CO2 Transport via Pipeline and Ship, www.ieaghg.org/docs/.../3._CO2_Transport_Overview_-_S._Santos_IEAGHG.pdf).
122. P. Noothout, F. Wiersma, O. Hurtado, P. Roelofsen and D. Macdonald, *CO2 Pipeline Infrastructure*, IEA Green- house Gas R&D Programme (IEAGHG), 2014.
123. X. Wang and M. M. Maroto-Valer, *127. ChemSusChem*, 2011, **4**, 1291-1300.
124. F. Bodénan, F. Bourgeois, C.Petiot, T. Augé, B. Bonfils, C. Julcour-Lebigue, F. Guyot, A. Boukary, J. Tremosa, A. Lassin, E. C. Gaucher and P. Chiquet, *Minerals Engineering*, 2014, **59**, 52-63.
125. A. Kirchofer, A. Becker, A. Brandt and J. Wilcox, *Environ. Sci. Technol.*, 2013, **47**, 7548–7554.
126. M.-G. Lee, D. Kang, Y. Yoo, H. Jo, H.-J. Song and J. Park, *Ind. Eng. Chem. Res.*, 2016, **55**, 11795-11800.
127. J. Artz, T. E. Müller, K. Thenert, J. Kleinekorte, R. Meys, A. Sternberg, A. Bardow and W. Leitner, *Chem. Rev.*, 2018, **118**, 434−504.
128. P. G. Jessop, S. M. Mercer and D. J. Heldebrant, *Energy Environ. Sci.*, 2012, **5**, 7240-7253.
129. Eugenio Quaranta and M. Aresta, *Carbon Dioxide as Chemical Feedstock* , Wiley-VCH, 2010.
130. G. Ma, J. Deng and M. P. Sibi, *Angew.Chem. Int. Ed.*, 2014, **53**, 11818-11821.
131. R. Csuk, A. Barthel, R. Kluge and D. Ströhl, *Bioorganic & Medicinal Chemistry*, 2010, **18**, 7252-7259.
132. Q. Ren, H. Xu, Q. Yu and S. Zhu, *Ind. Eng. Chem. Res.*, 2015, **54**, 11056–11064.
133. D. B. Dell'Amico, F. Calderazzo, L. Labella, F. Marchetti and G. Pampaloni, *Chem. Rev.*, 2003, **103**, 3857-3898.
134. L. Armelao, D. B. Dell’Amico, P. Biagini, G. Bottaro, S. Chiaberge, P. Falvo, L. Labella, F. Marchetti and S. Samaritani, *Inorg. Chem.*, 2014, **53**, 4861-4871.
135. D. C. Ducat and P. A. Silver, *Current Opinion in Chemical Biology*, 2012, **16**, 337-344.
136. E. M. Pineda, Y. Lan, O. Fuhr, W. Wernsdorfer and M. Ruben, *Chem. Sci.*, 2017 , **8**, 1178-1185.
137. T. M. McDonald, J. A. Mason, X. Kong, E. D. Bloch, D. Gygi, A. Dani, V. Crocellà, F. Giordanino, S. O. Odoh, W. S. Drisdell, B. Vlaisavljevich, A. L. Dzubak, R. Poloni, S. K. Schnell, N. Planas, K. Lee, T. Pascal, L. F. Wan, D. Prendergast, J. B. Neaton, B. Smit, J. B. Kortright, L. Gagliardi, S. Bordiga, J. A. Reimer and J. R. Long, *Nature*, 2015, **519**, 303-308.
138. M. Moss, D. G. Reed, R. W. K. Allen and P. Styring, *Front. Energy Res.*, 2017, **5**, 1-12.
139. L. Wang, Y. Yi, H. Guo and X. Tu, *ACS Catal.*, 2018, **8**, 90-100.
140. D. B. Lao, B. R. Galan, J. C. Linehan and D. J. Heldebrant, *Green Chem.*, 2016, **18**, 4871-4874

141. N. M. Rezayee, C. A. Huff and M. S. Sanford, *J. Am. Chem. Soc.*, 2015, **137**, 1028-1031.
142. W. Lu, B. Jia, B. Cui, Y. Zhang, K. Yao, Y. Zhao and J. Wang, *Angew. Chem. Int. Ed.*, 2017, **129**, 12013-12016.
143. J. Kothandaraman, A. Goeppert, M. Czaun, G. A. Olah and G. K. S. Prakash, *Green Chem.*, 2016, **18**, 5831-5838.
144. M. Scott, B. B. Molinos, C. Westhues, G. Franciò and W. Leitner, *ChemSusChem*, 2017, **10**, 1085-1093.
145. T. Ouyang, C. Hou, J.-W. Wang, W.-J. Liu, D.-C. Zhong, Z.-F. Ke and T.-B. Lu, *Inorg. Chem.*, 2017, **56**, 7307-7311.
146. H. Rao, L. C. Schmidt, J. Bonin and M. Robert, *Nature*, 2017, **548**, 74-77.
147. M. Mikkelsen, M. Jørgensen and F. C. Krebs, *Energy Environ. Sci.*, 2010, **3**, 43-81.
148. M. Arti, M. H. Youn, K. T. Park, H. J. Kim, Y. E. Kim and S. K. Jeong, *Energy Fuels*, 2017, **31**, 763-769.
149. K. S. Lackner, C. H. Wendt, D. P. Butt, E. L. J. Jr. and D. H. Sharp, *Energy*, 1995, **20**, 1153-1170.
150. J. M. Matter, M. Stute, S. Ó. Snæbjörnsdottir, E. H. Oelkers, S. R. Gislason, E. S. Aradottir, B. Sigfusson, I. Gunnarsson, H. Sigurdardottir, E. Gunnlaugsson, G. Axelsson, H. A. Alfredsson, D. Wolff-Boenisch, K. Mesfin, D. F. d. l. R. Taya, J. Hall, K. Dideriksen and W. S. Broecker, *Science*, 2016, **352**, 1312-1314.
151. P. Adams and F. A. Baron, *Chem. Rev.*, 1965, **65**, 567–602.
152. E. Bernoud, A. Company and X. Ribas, *J. Organomet. Chem.*, 2017, **845**, 44-48.
153. C. D. N. Gomes, O. Jacquet, C. Villiers, P. Thuéry, M. Ephritikhine and T. Cantat, *Angew. Chem. Int. Ed.*, 2012, **51**, 187-190.
154. Zhen-Zhen Yang, L.-N. He, J. Gao, A.-H. Liua and B. Yua, *Energy. Environ. Sci.* , 2012, **5**, 6602-6639.
155. A. H. Liu, R. Ma, C. Song, Z. Z. Yang, D. A. Yu, Y. Cai, L. N. He, Y. N. Zhao, B. Yu and Q. W. Song, *Angew. Chem. Int. Ed.*, 2012, **51**, 11306-11310.
156. W. McGhee, D. Riley, K. Christ, Y. Pan and B. Parnas, *J. Org. Chem.*, 1995, **60**, 2820-2830.
157. N. v. d. Assen, P. Voll, M. Peters and A. Bardow, *Chem. Soc. Rev.*, 2014, **43**, 7982-7994.
158. Y. Li, Z. Liu, R. Cheng and B. Liu, *ChemCatChem.*, 2018, **10**, 1420-1430.
159. R. Rodriguez, D. Gau, J. Saouli, A. Baceiredo, N. Saffon-Merceron, V. Branchadell and T. Kato, *Angew. Chem. Int. Ed.*, 2017, **56**, 3935-3939.
160. R. Angamuthu, P. Byers, M. Lutz, A. L. Spek and E. Bouwman, *Science*, 2010, **327**, 313-315.
161. S. J. Varma, K. B. Muchowska, P. Chatelain and J. Moran, *Nat. Ecol. Evol.*, 2018, **2**, 1019–1024.
162. W. Zhang, Y. Hu, L. Ma, G. Zhu, Y. Wang, X. Xue, R. Chen, S. Yang and Z. Jin, *Advanced Science*, 2018, **5**, 1700275.
163. T.-T. Zhuang, Z.-Q. Liang, A. Seifitokaldani, Y. Li, P. D. Luna, T. Burdyny, F. Che, F. Meng, Y. Min, R. Quintero-Bermudez, C. T. Dinh, Y. Pang, M. Zhong, B. Zhang, J. Li, P.-N. Chen, X.-L. Zheng, H. Liang, W.-N. Ge, B.-J. Ye, D. Sinton, S.-H. Yu and E. H. Sargent, *Nat. Cat.*, 2018, **1**, 421–428.
164. C. Xie, C. Chen, Y. Yu, J. Su, Y. Li, G. A. Somorjai and P. Yang, *Nano Lett.*, 2017, **17**, 3798–3802.
165. P. Gao, S. Dang, S. Li, X. Bu, Z. Liu, M. Qiu, C. Yang, H. Wang, L. Zhong, Y. Han, Q. Liu, W. Wei and Y. Sun, *ACS Catal.*, 2018, **8**, 571-578.
166. T. Haas, R. Krause, R. Weber, M. Demler and G. Schmid, *Nature Catalysis*, 2018, **1**, 32-39.
167. T. Schwander, L. S. v. Borzyskowski, S. Burgener, N. S. Cortina and T. J. Erb, *Science*, 2016, **354**, 900-904.
168. J. Wei, Q. Ge, R. Yao, Z. Wen, C. Fang, L. Guo, H. Xu and J. Sun, *Nat. Commun.*, 2017, **8**, 15174.
169. J. Ren, F.-F. Li, J. Lau, L. González-Urbina and S. Licht, *Nano Lett.*, 2015, **15**, 6142-6148.
170. A. Douglas, N. Muralidharan, R. Carter and C. L. Pint, *ACS Sustainable Chem. Eng.*, 2017, **5**, 7104-7110.
171. Y. Qiao, J. Yi, S. Wu, Y. Liu, S. Yang, P. He and H. Zhou, *Joule*, 2017, **1**, 359-370.