

## PAPER

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The Twelve Principles of CO<sub>2</sub> CHEMISTRY†Martyn Poliakoff,<sup>\*a</sup> Walter Leitner<sup>\*bc</sup> and Emilia S. Streng<sup>ab</sup>

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This paper introduces a set of 12 Principles, based on the acronym CO<sub>2</sub> CHEMISTRY, which are intended to form a set of criteria for assessing the viability of different processes or reactions for using CO<sub>2</sub> as a feedstock for making organic chemicals. The principles aim to highlight the synergy of Carbon Dioxide Utilisation (CDU) with the components of green and sustainable chemistry as well as briefly pointing out the connection to the energy sector.

## Introduction

The world is changing rapidly. The global population is soaring, passing 7 billion in October 2011.<sup>1</sup> Human consumption is already greater than our planet can sustain; furthermore, 1.3 billion of the Earth's inhabitants are profoundly poor and, on every criterion, deserve to consume more.<sup>2,3</sup> Therefore, there is a need to increase chemical production to match the increased demand. However, it is generally accepted that petroleum reserves are finite and that it is necessary to find alternative feedstocks for making those chemicals. Although the planet's reserves of coal are much larger than those of oil, it is not clear whether these could be exploited to make chemicals without the release of large quantities of CO<sub>2</sub>. Shale gas provides another large volume carbon source and, although its exploitation is associated with a large potential environmental burden, it is having a major impact on chemical production, often causing a shift from petroleum feedstocks. Nevertheless, the utilization of all fossil resources ultimately contributes to anthropogenic greenhouse gas emissions, either directly (methane) and/or indirectly by producing CO<sub>2</sub> as the end product of the value chain.

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† Dedicated to the memory of our dear Nottingham colleague, Professor Daniel D Eley OBE FRS FRSC, the elder statesman of catalysis worldwide, who died peacefully on Sept 3rd, four days before the start of this Faraday Discussion and four weeks short of his 101<sup>st</sup> birthday.



Already, CO<sub>2</sub> levels are the highest in recorded history and there is a general scientific consensus that further increases in atmospheric CO<sub>2</sub> will have serious consequences for the Earth's climate.<sup>4-6</sup> The global demand for energy is rapidly increasing and CO<sub>2</sub> emissions are not yet under control. Therefore, all efforts have to be undertaken to reduce these emissions in every industrial sector including the production of chemicals.

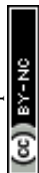
A highly attractive scenario in this context is to make chemicals from CO<sub>2</sub>, either captured before it is emitted to the atmosphere or by recovering it from the atmosphere *via* photosynthesis in biomass or *via* some equivalent artificial process. That is not to say that making chemicals from CO<sub>2</sub> could mitigate anthropogenic emissions of CO<sub>2</sub> because the scales of the two activities are totally mismatched: global CO<sub>2</sub> emissions are in the order of 10<sup>10</sup> tons p.a. while the maximum potential consumption of CO<sub>2</sub> in chemical and industrial processes is estimated as 10<sup>8</sup> tons p.a.<sup>7</sup> So, even allowing for possible errors, these numbers are never likely to match.

However, these data can be seen as encouraging, rather than frustrating; they clearly indicate that CO<sub>2</sub> is and will be available from various industrial sources in more than sufficient quantities for its intensive use as chemical feedstock in Carbon Dioxide Utilisation (CDU). Capturing CO<sub>2</sub> from highly concentrated sources, *e.g. via* processes such as those developed for Carbon Capture and Storage (CCS) technologies,<sup>8</sup> may well provide an excellent source of CO<sub>2</sub> for making chemicals at least in the short to medium term. On the other hand, even if chemical processes require comparatively small amounts of CO<sub>2</sub> compared to the possible output of CCS, CDU does have the potential to add value to captured CO<sub>2</sub> which would otherwise be a largely valueless waste product. The idea of using CO<sub>2</sub> as a feedstock has fascinated chemists for decades, as indicated for example by the more than 20 years history of the International Conference on Carbon Dioxide Utilization (ICCDU). Potential synergies at the interface between chemistry and energy and the resulting opportunities for viable technical solutions associated with CDU have been a topic of lively discussion at this Faraday Discussion.

This Faraday Discussion includes 22 papers, apart from this one and the Concluding Remarks. The purpose of this introductory paper is to present a check list of the 12 Principles of CO<sub>2</sub> Chemistry to provide a rough set of metrics for gauging the value of a particular proposal in this area. The inspiration is the now

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|---|---------------------------------------|
| C | Catalysis is crucial                  |
| O | Origin of the CO <sub>2</sub> ?       |
| 2 | Tomorrow's world may be different     |
| C | Cleaner than existing process?        |
| H | High volume or high value products?   |
| E | E-factor must be low                  |
| M | Maximize integration                  |
| I | Innovative process technology         |
| S | Sustainability is essential           |
| T | Thermodynamics cannot be beaten       |
| R | Renewable (& reasonable) energy input |
| Y | Your enthusiasm is not enough         |

Fig. 1 The proposed 12 Principles of CO<sub>2</sub> Chemistry. Their meaning is explained in the text.



widely known 12 Principles of Green Chemistry, introduced in 1998 by Anastas and Warner, which has now become an almost standard means of assessing green processes.<sup>9</sup> However, it has to be admitted that the full statement of the principles is quite lengthy. So, more recently, a condensed version of these principles was introduced, based on the acronym PRODUCTIVELY, to provide a list that could conveniently (and legibly) be shown on a single PowerPoint slide.<sup>10</sup>

Here we provide an equivalent condensed list for CO<sub>2</sub> CHEMISTRY in the hope that it will help to highlight the most pertinent issues and to structure future discussions of CDU. The list is shown in Fig. 1 as it was presented in the Introductory Lecture and below we expand these principles and explain how they might be applied.

## Catalysis is crucial

CO<sub>2</sub> is notoriously unreactive in organic synthesis and in reductive processes. It can be considered a thermodynamic minimum with only highly energy rich compounds being able to react with it. Such reactions do not necessarily require a catalyst. For example, once heated, magnesium metal reacts with CO<sub>2</sub> in a highly exothermic reaction<sup>11</sup> ( $2\text{Mg} + \text{CO}_2 \rightarrow 2\text{MgO} + \text{C}$ ) but the reaction yields elemental carbon which is not necessarily a useful starting point for making chemicals, especially given the financial and energy costs of obtaining metallic magnesium. Thus, nearly all reactions for making chemicals from CO<sub>2</sub> really need to use catalysts.<sup>12,13</sup> Heterogeneous catalysts are able to promote important transformations of carbon dioxide such as the famous Sabatier reaction  $\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$ .<sup>14</sup> Homogeneous catalysts are very selective for many synthetically useful C–C and C–X bond formation processes.<sup>15,16</sup> Electro- and photochemical transformations of CO<sub>2</sub> also require suitable catalyst materials or molecular catalysts due to the large over-potential for CO<sub>2</sub> reduction to its radical anion.<sup>17</sup> Nature's ingenious catalytic processes for construction of its entire material basis from CO<sub>2</sub> can serve as motivation to develop man-made catalysts for industrial implementation.

## Origin of the CO<sub>2</sub>?

CO<sub>2</sub> can be sequestered from many industrial processes and other sources.<sup>18</sup> The need for catalysis may well place quite severe restrictions on the purity of the CO<sub>2</sub>. Trace impurities could easily poison catalysts or oxidize expensive ligands. Fortunately, the large disparity between global CO<sub>2</sub> production and the possible consumption by the chemical industry means that operators of chemical processes can afford to be quite choosy about the source of their CO<sub>2</sub>. For example, some processes may require relatively dry CO<sub>2</sub> and could benefit from fears of pipeline corrosion in CCS that are leading to relatively stringent proposals for acceptable levels of H<sub>2</sub>O currently for any captured CO<sub>2</sub> to be transported by pipeline.<sup>19</sup> At the same time, using atmospheric CO<sub>2</sub> will always carry a large energy cost because of the need to move very large masses of air to obtain a sufficient flux of CO<sub>2</sub> through one's chemical process. It may well be hard to beat photosynthesis by plants/trees/algae as a means of deriving carbon compounds from the atmosphere, even though such photosynthesis often requires very large amounts of fresh water, a commodity that may well be in short supply in the



future. Furthermore if a process is based on sequestration of CO<sub>2</sub> by formation of biomass, one needs to consider questions of land usage, of “food *versus* chemicals” as well as water usage, all of which impact the overall sustainability.<sup>20</sup>

## Tomorrow's world may be different

Unlike academic research, commercial chemical manufacture has to face economic reality. This means that any CO<sub>2</sub>-based process will be fully exposed to changes in the financial environment. Government subsidies can change rapidly with changes of government or policy. In this context it is important to remember that, although CO<sub>2</sub>-based chemistry cannot make a significant impact on overall anthropogenic CO<sub>2</sub> emissions, it could reduce the emissions from a particular plant or company; such a reduction could give a significant fiscal advantage to that company. Also, the global oil price, which is a key parameter in determining the commercial viability of any CO<sub>2</sub>-based process, can fluctuate widely; for example the price of Brent Crude has dropped by nearly 50% over the last 12 months,<sup>21</sup> gravely affecting the economics of otherwise attractive processes using alternative carbon sources. On the other hand, the possibility of providing an outlet for fluctuating “excess” renewable energy could constitute a novel, quite unexpected business opportunity in the future.<sup>22,23</sup> Hence, the distinction between economically “useful” or “useless” processes is likely to depend on time and place, leading to different strategies when devising short-term and long-term goals in science.

## Cleaner than existing process?

Just like in any chemical process, “greenness” should be an *a priori* criterion for CO<sub>2</sub> Chemistry: it seems only sensible that any new process should be cleaner (or at least not dirtier) than any existing process that it replaces. This is more than a mere gesture towards environmentalism. Disposal of waste has become a significant and increasing cost for chemical producers and the more toxic the waste, the more expensive is its disposal. Importantly, CO<sub>2</sub> holds great potential also in this context; it is a non-toxic, safe reagent as compared to many other C1-building blocks, often producing water as the only by-product. Ideally, the energetic and material aspects of the “green” approach work together to minimize both energy requirements and the waste produced, and it can be a very difficult task to balance the benefits and drawbacks if this is not the case.<sup>24</sup>

## High volume or high value products?

This is an absolutely key question. If one is aiming to make high volume/low value products, any CO<sub>2</sub>-based process must necessarily be low cost, thereby removing the option of using expensive catalysts or other costly processing options. Such processes will also be particularly vulnerable to fluctuations in the price of oil because feedstock price will be a large proportion of the cost of the final product. Conversely, if one is making low volume/high value products, the price of the feedstock will be only a small component in the overall cost and so any cost advantage of CO<sub>2</sub> as a feedstock may only be marginal. An attractive option, therefore, may be to aim for medium volume/medium value products where the



cost of the feedstock is significant but low enough to dampen out effects of temporary swings in the oil price. A good example described below is the CO<sub>2</sub>-based production of polyols for the manufacture of polyurethane polymers, which is currently being implemented on industrial scale in Germany.<sup>25,26</sup>

## E-factor must be low

One of the key concepts of Green Chemistry is the E factor, originally proposed by Sheldon.<sup>27</sup> The factor is the weight of waste generated per unit weight of product. Its use has had real impact on chemical production, for example resulting in huge reductions in solvent usage in the production of Viagra.<sup>28</sup> However, it has even more importance in CO<sub>2</sub>-based chemistry. This is because conversion of CO<sub>2</sub> into organic compounds is energy intensive and therefore waste organic compounds will also represent a waste of energy. In the introductory lecture, the Braskem process for making polyethene from cane sugar was mentioned, as an example of using CO<sub>2</sub> *via* photosynthesis.<sup>29,30</sup> The subsequent chemistry is simple: sucrose is fermented to ethanol, which is dehydrated to ethene that is then polymerized. The advantage is that the product slots into existing supply chains without the need to create a new commercial infrastructure. As regards the E-factor, 33% of the carbon fixed by photosynthesis is released as CO<sub>2</sub> during the fermentation (and, like all CO<sub>2</sub> utilization processes, it is vulnerable to falling oil prices which can render the cost of the product uncompetitive).

## Maximize integration

Although research in CCS and research in CDU have often been carried out separately, it clearly makes sense to integrate carbon capture and its subsequent use. We have previously described how captured CO<sub>2</sub> might be exploited as a solvent for reactions in supercritical CO<sub>2</sub>.<sup>31</sup> The rationale is that the energy costs of compressing CO<sub>2</sub> represent a substantial fraction of the cost of supercritical processing; however, compression of CO<sub>2</sub> is an integral part of the capture and transport technology. Consequently, power plants or industrial processes equipped with capture units could provide high pressure CO<sub>2</sub> at no or moderate additional cost. Although a supercritical CO<sub>2</sub> solvent is not strictly “utilised”, because the CO<sub>2</sub> is still there at the end of the process, it could represent a substantial reduction in the usage of petroleum-based materials as solvents. A more chemically elegant example of integration is the process developed jointly by Bayer together with the CAT Catalytic Center at RWTH Aachen, which is now being commercialised by the company Covestro.<sup>25</sup> The catalytic transformation has been demonstrated to be compatible with captured CO<sub>2</sub> even from coal fired power plants and other processes; the process is now being industrialised with production using the CO<sub>2</sub> by-product from an ammonia synthesis plant located on the same industrial site. A Life Cycle Assessment is described in one of the papers in this Discussion (DOI: 10.1039/c5fd00067j).

## Innovative process technology

Many proposed CO<sub>2</sub>-based processes will require new chemical plants to implement them, immediately adding capital expenditure to other start-up costs.



Therefore, the introduction of innovative process technology, particularly continuous processing could have a significant impact on the economics of the process. The synthesis of formic acid from  $\text{CO}_2$  and  $\text{H}_2$  provides an illustrative example, where the thermodynamics of the reaction require additional stabilization of the product in the reaction stage that needs to be overcome during the downstream product separation.<sup>32,33</sup>

## Sustainability is essential

Long term sustainability is a major reason, if not *the* major reason, for developing  $\text{CO}_2$ -based chemistry. Therefore, it has to be a criterion for judging the viability of any proposed process. However elegant the catalysis, one must always look at the whole life cycle; the energy and/or chemical resources needed to make the catalyst may well reveal that an otherwise attractive process is totally unsustainable. Furthermore, it is important to stress that sustainability involves more than demonstrating that a particular catalyst is based on abundant and easily obtained elements. Although the sustainability of a process can only be reasonably established by Life Cycle<sup>34</sup> or similar assessments (DOI: 10.1039/c5fd00038f), which are quite lengthy procedures, it may often be easier and quicker to recognize processes that are obviously unsustainable.

## Thermodynamics cannot be beaten

As in other areas of chemistry, the thermodynamics of  $\text{CO}_2$ -based processes depend on where one draws the system boundary. For example, the hydrogenation of  $\text{CO}_2$  mentioned above,  $\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$ , is exothermic, provided that one does not consider the energy involved in generating the hydrogen. Thermodynamics assume that systems are in equilibrium. Therefore, although thermodynamics cannot be beaten, it may be possible to side-step thermodynamic barriers by deliberately avoiding equilibrium situations, for example in plasma processing (DOI: 10.1039/c5fd00053j and DOI: 10.1039/c5fd00045a). Furthermore, even an endothermic process using  $\text{CO}_2$  can be advantageous, if the alternative routes consume even more energy to arrive at the same product or function. This emphasises again that one must consider the whole system with clearly defined boundary conditions in making an evaluation, and most evaluations are only valid in comparison, rather than as absolute values.

## Renewable (& reasonable) energy input

Since the aim of  $\text{CO}_2$  Chemistry is to avoid use of fossil carbon in the manufacture of chemicals, it is clearly not sensible to incorporate less  $\text{CO}_2$  into the chemicals than one creates by burning fossil carbon to generate the energy needed to make those chemicals. Otherwise, one might as well start with the fossil carbon as the feedstock. Therefore, renewable energy might seem to be the panacea for  $\text{CO}_2$ -based chemistry. If renewable energy sources are coupled with  $\text{CO}_2$  as the carbon source, this could decouple the carbon emission from the energy sector and the feedstock.<sup>22,23</sup> Of course, this does not eliminate the challenge of devising energy efficient processes. Also renewable energy will not be “for free”, either economically or environmentally. Furthermore, if renewable energy does become available



on large scales, the chemical industry will not be the only potential outlet and its use may have an even larger impact on our carbon emissions in other sectors. Hence, the goal of minimizing the energy requirements of chemical production remains a core issue in CO<sub>2</sub> Chemistry, regardless of the primary energy source.

## Your enthusiasm is not enough

In the context of this Discussion, the purpose of CDU is to devise processes that can lead to viable methods of using CO<sub>2</sub> as a chemical feedstock. Therefore, one needs to apply a certain degree of realism to any proposed CDU process whatever its intellectual and academic fascination. This is not to say that successful CDU processes will be mundane or boring. Merely, it means that processes will have the best chance of success if they arouse widespread interest, not only in academia but amongst those who make chemicals to sell. Even so, it must be stressed that society is wider than either academia or industry. Ethical issues and environmental consequences as well as the aesthetic impact on the landscape are also important, if not paramount issues. These are also issues that are strongly championed by non-governmental organizations (NGOs) and other lobby groups. Therefore, it is salutary to remember that no process, however elegant and potentially profitable, will be genuinely sustainable without the positive support from the wider community.

## Conclusions

Humanity faces enormous challenges over how to maintain our quality of life as this century progresses. We face the threat of multiple shortages, increasing concentrations of greenhouse gases in the atmosphere, dwindling oil supplies, and increasingly expensive chemicals. CDU represents an excellent opportunity to reduce our dependency on fossil resources for making the chemicals that we will need for the foreseeable future. It also offers the possibility of harvesting renewable energy to benefit the chemical value chain. This possibility places CDU right at the interface between chemistry and energy.

The 12 Principles outlined here are intended to focus attention on the key issues that need to be addressed if CDU is to succeed in the way in which all of the participants in this Faraday Discussion hope. Those participants included both chemists and chemical engineers working on all aspects along the value chain. Success requires partnership across disciplinary boundaries. It is not guaranteed but it will not come if we do not all work together towards a common aim. In the longer term, it is the role of CO<sub>2</sub> Chemists and Engineers to get societal support for our joint endeavours so that our vision of sustainable CO<sub>2</sub>-based chemical manufacture for the future can be fully realized.

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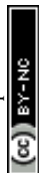
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